Superhydrophobic SERS substrates based on silicon hierarchical nanostructures

Xuexian Chen¹, Jinxiu Wen¹,², Jianhua Zhou³, Zebo Zheng¹, Di An¹, Hao Wang¹,², Weiguang Xie⁴, Runze Zhan¹, Ningsheng Xu¹, Jun Chen¹, Juncong She¹, Huanjun Chen¹,²,⁵,⁶ and Shaozhi Deng¹,⁵

¹State Key Laboratory of Optoelectronic Materials and Technologies, Guangdong Province Key Laboratory of Display Material and Technology, School of Electronics and Information Technology, Sun Yat-sen University, Guangzhou 510275, People’s Republic of China
²School of Physics, Sun Yat-sen University, Guangzhou 510275, People’s Republic of China
³Key Laboratory of Sensing Technology and Biomedical Instruments of Guangdong Province, School of Engineering, Sun Yat-sen University, Guangzhou 510006, People’s Republic of China
⁴Siyuan Laboratory, Department of Physics, Jinan University, Guangzhou 510632, People’s Republic of China

E-mail: chenhj8@mail.sysu.edu.cn and stsdsz@mail.sysu.edu.cn

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Abstract

Silicon nanostructures have been cultivated as promising surface enhanced Raman scattering (SERS) substrates in terms of their low-loss optical resonance modes, facile functionalization, and compatibility with today’s state-of-the-art CMOS techniques. However, unlike their plasmonic counterparts, the electromagnetic field enhancements induced by silicon nanostructures are relatively small, which restrict their SERS sensing limit to around 10⁻⁷ M. To tackle this problem, we propose here a strategy for improving the SERS performance of silicon nanostructures by constructing silicon hierarchical nanostructures with a superhydrophobic surface. The hierarchical nanostructures are binary structures consisted of silicon nanowires (NWs) grown on micropyramids (MPs). After being modified with perfluoroctyltriethoxysilane (PFOT), the nanostructure surface shows a stable superhydrophobicity with a high contact angle of ∼160°. The substrate can allow for concentrating diluted analyte solutions into a specific area during the evaporation of the liquid droplet, whereby the analytes are aggregated into a small volume and can be easily detected by the silicon nanostructure SERS substrate. The analyte molecules (methylene blue: MB) enriched from an aqueous solution lower than 10⁻⁸ M can be readily detected. Such a detection limit is ∼100-fold lower than the conventional SERS substrates made of silicon nanostructures. Additionally, the detection limit can be further improved by functionalizing gold nanoparticles onto silicon hierarchical nanostructures, whereby the superhydrophobic characteristics and plasmonic field enhancements can be combined synergistically to give a detection limit down to ∼10⁻¹¹ M. A gold nanoparticle-functionalized superhydrophobic substrate was employed to detect the spiked melamine in liquid milk. The results showed that the detection limit can be as low as 10⁻⁵ M, highlighting the potential of the proposed superhydrophobic SERS substrate in practical food safety inspection applications.

5 Authors to whom any correspondence should be addressed.
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(Some figures may appear in colour only in the online journal)

1. Introduction

Surface enhanced Raman scattering (SERS) is among the most promising techniques for noninvasive, non-labeling, fingerprint-type, and trace-amount sensing applications [1–4]. The utilization of the SERS technique into practical applications of biosensing and chemical sensing strongly relies on robust, reliable, and low-cost substrates with outstanding Raman amplification. To date the prevailing SERS substrates are noble metal nanostructures, such as gold (or silver) nanoparticles, nanostructured island films, and complex architectures fabricated with microfabrication techniques [5–8]. These nanostructures exhibit excellent SERS activity due to their plasmon resonances. On the other hand, in recent years, silicon nanostructures (such as NWs, nanopillars, and nanoparticles) have attracted more and more research interest because of their low-loss optical resonances in the visible region, which can give rise to strong light scattering [9, 10]. Silicon nanostructures are therefore cultivated as promising SERS substrates [11, 12]. Moreover, for practical device applications, the excellent semiconducting properties and compatibility with today’s state-of-the-art CMOS techniques make silicon nanostructures superior to their metallic counterparts. For these reasons, it is foreseen that silicon nanostructures have opened up new avenues for novel SERS substrates that are complementary to the traditional plasmonic metal nanostructures [13, 14].

However, the electromagnetic field enhancements induced by silicon nanostructures are usually smaller than their plasmonic counterparts [15], which strongly limit their SERS activity and therefore hinder their applications in bio- and chemical ultratrace sensing. To improve the SERS performances of silicon nanostructures, one can functionalize them with noble metal nanoparticles to form hybrid structures. By taking advantage of the synergistic interactions between the dielectric and metal components, the near-field electromagnetic fields can be significantly enhanced, which therefore improve the SERS activity of silicon nanostructures. For example, it has been reported that silicon NWs functionalized with metal nanoparticles could serve as a highly-efficient SERS substrate for ultrasensitive chemical and biomolecules detection [16–19]. On the other hand, one can also construct SERS substrates with superhydrophobic surfaces to overcome the ‘diffusion limit’ of analytes in highly diluted aqueous solution. In such a manner, the analyte molecules within an evaporating liquid droplet can be concentrated into a specific region with very small area onto the SERS substrate [20–23]. Due to the enrichment of the analytes, ultrasensitive detection in aqueous solvents of very low concentrations can thereafter be achieved by using the superhydrophobic substrates with relatively low electromagnetic field enhancements. Although this strategy has been demonstrated as the most successful way of improving the sensitivity of the plasmonic-type SERS substrates [24], similar studies remain unexplored in the SERS substrates made up of pure silicon nanostructures.

In this study, we attempt to improve the SERS activity of silicon nanostructures by constructing superhydrophobic surfaces consisting of silicon hierarchical nanostructures. The hierarchical nanostructures with silicon NWs grown on micropyramids (MPs) were obtained using wet-chemical etching method. Stable superhydrophobic surfaces, which were then employed as SERS substrates, could be realized by functionalizing the hierarchical structures with PFOT. The detection limit for the substrate can be smaller than $10^{-8}$ M with methylene blue (MB) as probe molecules, which is ~100-fold lower than the conventional silicon SERS substrates. Such a detection limit can be further improved to $10^{-11}$ M by functionalizing the superhydrophobic silicon substrates with plasmonic gold nanoparticles. To demonstrate the real-life applications of the proposed substrates, we showed that a gold nanoparticle-functionalized superhydrophobic silicon nanostructure can be utilized to detect the spiked melamine in liquid milk, with a detection limit down to $10^{-5}$ M. We strongly believe that our studies can pave the way for greatly furthering the development of silicon-based SERS substrates in future applications of biosensing, chemical sensing, diagnostics, and food safety inspection.

2. Methods

2.1. Materials

1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOT, 98%), silver nitrate (AgNO$_3$, 99.5%), melamine (99%), and MB were purchased from Sigma–Aldrich. Toluene (99.9%) was purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd. The liquid milk was a commercial product purchased from a supermarket. Deionized water was used for all of the experiments.

2.2. Fabrication of the silicon hierarchical nanostructures

The silicon hierarchical nanostructures consisted of MP and NW binary architectures and were obtained by a two-step etching process (figure 1). Firstly, the single-crystalline silicon wafer was cleaned consecutively for 15 min in acetone, ethanol, and deionized water, respectively, followed by drying with N$_2$ flow. The MPs were fabricated by immersing a silicon wafer into a mixture of ethanol (10 vol.%) and NaOH (2 w.%) at 80 °C for 30 min [25, 26]. After being rinsed with an HCl solution (0.1 M) to remove the residual NaOH, the silicon MP substrate was immersed into the HF solution (5 w.%) to remove the oxide layer formed during the above processes. In the second step, silicon NWs were grown onto
the MPs by metal-assisted chemical etching [27, 28]. Briefly, the silicon MPs were immersed into a solution mixed with HF (4.8 M) and AgNO₃ (0.02 M). The etching lasted for 5 min at room temperature to grow the silicon NWs on the silicon MPs. The obtained product was dipped into a HNO₃ solution (30 wt.%) for 1 h to completely remove the residual Ag. Afterwards, the sample was rinsed with copious amounts of deionized water and dried with N₂.

### 2.3. Preparation of the superhydrophobic SERS substrates

The as-grown silicon hierarchical nanostructures were placed in a 400 μl toluene solution containing 100 μl PFOT for fabrication of the superhydrophobic substrates. The substrates were then kept at room temperature for 8 h (figure 1). Before the SERS characterizations, the substrates were dried naturally under ambient condition.

### 2.4. Preparation of the liquid milk sample for melamine detection

Liquid milk with 10⁻⁵ M of spiked melamine was purified according to a procedure reported previously [29]. Specifically, HCl (200 μl, 1 M) was added to 4 ml of the liquid milk and mixed by inversion. Afterwards, the solution was centrifuged at 104 rpm for 30 min, followed by filtering the supernatants using a 0.22 μm polytetrafluoroethylene filter. The filtered solution was then mixed with the NaOH (60 μl, 1 M). Similar centrifugation and filtration processes were then conducted. For the subsequent SERS characterizations, 10 μl of the obtained solution was drop-casted onto the superhydrophobic substrate (figure 1).

### 2.5. Functionalization of the silicon hierarchical SERS substrates with gold nanoparticles

To functionalize gold nanoparticles onto the silicon hierarchical SERS substrates (figure 1), gold metal was sputtered onto the binary structures at room temperature using a desktop DC sputtering system (Q150TS of Qurum Technologies). The operation chamber pressure was 5 Pa. The sputtering lasted for 200 s at a working current of 2 mA. The substrates were subsequently subjected to thermal annealing at 570 °C for 1 h to obtain the gold nanoparticles. The hierarchical nanostructures functionalized with gold nanoparticles were then immersed into the PFOT solution to get a superhydrophobic surface (figure 1).

### 2.6. Characterizations

The morphologies and crystalline structures of the silicon hierarchical nanostructures were characterized using scanning electron microscope (SEM) and transmission electron microscope (TEM), respectively. The SEM imaging was conducted on an FEI Quanta 450 FEG microscope with an accelerating voltage of 10 kV. The high-resolution TEM (HRTEM) measurements were performed using an FEI Titan3 G2 60-300 microscope operating at 300 kV. Static contact angles (CAs) were measured at room temperature using the SL200B system (Kino, America). Specifically, water droplets (4 μl each) were dropped onto the as-prepared substrate, followed by measuring the average CAs from three different positions on the sample surface.

SERS measurements were conducted on a Renishaw inVia Reflex confocal micro-Raman system equipped with a dark-field microscope (Leica). Excitation lasers of 532 nm and 785 nm were employed for the measurements. The laser was focused onto the samples with a spot size of ~1 μm in diameter through an objective (Leica, 50×, numerical aperture: 0.75). The backscattered Raman spectra were collected via the same objective. For evaluating the SERS activity of the hierarchical nanostructures, MB and Rhodamine 6 G (R6G) molecules were used as probes. Specifically, 8 μl molecular aqueous solutions of different concentrations were drop-casted onto the superhydrophobic substrate. The droplets were then evaporated naturally under ambient conditions. Afterwards the SERS spectra were acquired using the 532 nm or 785 nm laser excitation, with an accumulation time of 10 s and a laser power of 0.54 mW. For detecting the melamine, a 785 nm laser was employed for the excitation. The accumulation time was 50 s and the laser power was 3.62 mW. Optical absorption spectrum was recorded with a UV–vis-NIR spectrophotometer (HITACHI U-4100).
Numerical simulations were carried out using a finite-difference time-domain (FDTD) method (Lumerical). The dielectric functions of the silicon and gold were taken from the literature [30]. To simplify the analysis, we only calculated the optical response of an individual silicon NW. In such a manner, the electromagnetic coupling between different NWs was neglected. This is reasonable because the separations between different NWs on the MPs were large enough to avoid the coupling effect (see the following discussions). To simulate the optical responses of the gold nanoparticle-functionalized hierarchical nanostructures, the nanoparticles were distributed uniformly onto the silicon NW surface with intimate contact. According to their average values obtained from the SEM and TEM characterizations, the diameters of the gold nanoparticles were set as 5 nm. The separation between the adjacent nanoparticles was 10 nm. The diameter of the silicon NW was 150 nm, and the length was set as 750 nm. The refractive index of the surrounding environment was 1.0.

A linearly polarized plane wave with a wavelength of 532 nm was launched towards the nanostructure. Perfectly matched layers were applied around the simulation region to absorb scattering radiation. Fine meshes were used for the nanostructure and its surroundings.

2.7. Numerical simulations

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3. Results and discussion

The hierarchical nanostructures consisted of silicon NWs sparsely grown on the MPs (figures 2(a) and (b)). The MPs exhibited base lengths of 5 ~ 10 μm and heights of 3 ~ 8 μm. The lengths and diameters of the NWs are 0.5 ~ 1 μm and 50 nm ~ 500 nm, respectively (figures 2(b) and (c)). The separations between the adjacent NWs are estimated to be ~200 nm. HRTEM imaging indicated that the silicon NWs are polycrystalline, with several growth directions within an individual NW (figure 2(d)). This is unexpected because the silicon wafer used for the growth of the nanostructures is single crystalline. We speculate that the formation of the polycrystalline silicon NWs is due to lattice reconstruction during the chemical etching process. The etching with the HF is usually violent, which can lead to defects and dislocations during growth of the NWs. In such a manner, the silicon lattices can undergo reconstructions, which lead to the polycrystalline structures of the obtained NWs.

The wettability of a specific surface is usually determined by its geometry and chemical properties [31]. Due to the hierarchical structures (figure 3(a)), the as-prepared substrates are an intrinsic hydrophobic surface, which is similar to the lotus leaf. When a water droplet was used for evaluating the surface wettability, the pristine silicon hierarchical nanostructures exhibit a CA of 89° ± 2° (figure 3(b)). The surface energy of the hierarchical nanostructures could be strongly reduced by functionalization with the PFOT molecules (figure 3(c)). As a result, the CA can be increased to 162° ± 1° (figure 3(d)), suggesting that the silicon hierarchical nanostructures modified with the PFOT become a superhydrophobic substrate.

For the SERS characterizations, 5 μl MB aqueous droplets of different concentrations were dropped onto the superhydrophobic silicon hierarchical nanostructure substrate. The substrate was able to confine the molecular solution within a small liquid–solid contact area. In contrary, the droplet spread across the entire nanostructure substrate without the PFOT functionalization. During its evaporation, the droplet always maintained the large CA on the substrate. Meanwhile, the droplet collapsed into a small area whereby the precipitate was found to aggregate onto the surface (figure 4(a)). In such a manner, the MB molecules were...
confined into a very small region, which acted as the actual site for the subsequent SERS measurements.

Prior to the SERS characterizations, we measured the Raman spectrum of the pristine MB (figure S1, the supporting information is available online at stacks.iop.org/JOPT/20/024012/mmedia). The Raman band at 1620 cm\(^{-1}\) which is assigned to the aromatic C–C stretching vibration is the strongest one [32]. Its intensity overwhelms those of the other modes. We therefore selected this mode for characterizing the SERS activities of the various substrates used in our study. The Raman spectra collected from the pristine and superhydrophobic silicon hierarchical nanostructure substrates are shown in figures 4(b) and (c). At high molecular concentrations, a characteristic Raman band at 1620 cm\(^{-1}\) could be observed from both of the substrates, which is assigned to the C–C stretching vibration of the MB molecule (table S1, supporting information). The two substrates exhibited quite different responses towards reduced molecular concentrations. For the pristine one, the dye droplet spreads across a large area on the substrate. The molecular concentration on a specific position of the substrate is very low. As a result, the Raman signal from this position will therefore be large. As a result, the C–C stretching vibration mode can be well-resolved from the noise background even when the MB concentration is down to \(10^{-9}\) M (figure 4(c) and figure S2(b), supporting information). To the best of our knowledge, such performance is the highest among the non-metallic SERS substrates (\(10^{-4} \sim 10^{-2}\) M) [33–35]. Therefore, the SERS activity of silicon nanostructures can be greatly improved by constructing hierarchical nanostructures of superhydrophobic surface. One should note that for these two substrates, there are additional Raman bands at 1300, 1370, and 1450 cm\(^{-1}\). These bands are not the characteristic fingerprints of MB molecules (table S1, supporting information). Their intensities are also dependent on the molecular concentrations. The origins of these bands are not clear yet. However, we believe that they are due to the underlying silicon substrate, which has also been reported previously [5]. As shown in the Raman spectra collected from the pristine silicon substrate and hierarchical silicon nanostructures (figure S3, supporting information), both substrates exhibit strong Raman bands at these three positions. Because no molecules were coated onto these two substrates, these three bands should not be stemmed from the molecules, but from the substrates themselves. In the SERS characterizations, upon reduction of the MB molecular concentrations, the

Figure 4. SERS characterizations of the silicon hierarchical nanostructure substrates. (a) Digital images showing the evaporation of a dye droplet (MB, 5 \(\mu\)l, 0.1 \(\mu\)M) on the superhydrophobic substrate. Scale bars: 20 \(\mu\)m. (b), (c) SERS spectra of the MB molecules at different concentrations collected from the pristine and superhydrophobic hierarchical nanostructure substrates, respectively.
broad background was suppressed. As a result, the signals from these three bands should be reduced as well.

The SERS activity of the dielectric substrates can be further improved by forming metal–dielectric hybrid nanostructures, whereby tremendous optical field enhancements can be generated by taking advantage of the electromagnetic coupling between the metal and dielectric components [36]. To that end, the substrate was deposited with gold nanoparticles. The substrate still maintained its superhydrophobic and hierarchical characteristics upon the metal deposition (figures 5(a)–(c) and figure S4, supporting information). The silicon NWs are densely covered with spherical gold nanoparticles. The diameters of the nanoparticles are 5 (±1.0) nm. The nanoparticles are either single crystalline or polycrystalline. For the single-crystalline ones, the interplanar spacing is 0.23 nm, which corresponds to the separation of the (111) plane (figure 5(d)).

The SERS capability of the superhydrophobic hybrid substrate was also evaluated using MB as probes. As expected, the hybrid substrate showed improved SERS performance in comparison with the pristine one. The Raman signals were still detectable for molecular concentrations down to 10^{-11} M (figure 6(a) and figure S5, supporting information). To further determine the detection limit of these two types of SERS substrates, a series of Raman spectra were collected with reduced molecular concentrations. As shown in figure 6(b), both substrates exhibited linear dependence on the Raman intensities (at 1620 cm^{-1}) on the logarithm (to the base of 10) of the molecular concentration. The detection limit of the hybrid substrate was almost two orders of magnitude higher than that of the pristine one. In addition, the hybrid structure exhibited a larger slope than the pristine substrate, suggesting a higher sensitivity for SERS detection. The superior Raman enhancement from the hybrid substrate can be ascribed to the additional electric field enhancement induced by the electromagnetic coupling between the silicon NW and the gold nanoparticles. The gold nanoparticles were closely adhered to the silicon NW surfaces, whereby the charge oscillations in the metal and dielectric could interact strongly with each other under external excitation. As a result, the electric fields can be enhanced remarkably on the surfaces of the metal and the NWs, as well as the contact regions between them (figure 6(c)). Such a mechanism gives rise to the excellent SERS activity of the hybrid substrate.

One should note that there is another origin for the SERS activities observed in our study, which is the resonance Raman effect induced by electronic transition between different states in the MB molecules. To unveil such an effect we measured the absorption spectrum of the MB molecules (figure S6, supporting information). The absorption maximum of the MB molecules locates at 662 nm, which is far away from the excitation laser of 532 nm. Therefore, the incidence light will not initiate the electronic transition in the molecules. As a result, we believe that the resonance Raman effect should contribute little to the SERS activities.

The SERS activity of the superhydrophobic hierarchical silicon nanostructures can be generalized to other probe molecules. To that end, we have characterized the SERS performances of the superhydrophobic silicon hierarchical nanostructures with the R6G molecules. In comparison with the pristine hierarchical nanostructures, the superhydrophobic hierarchical nanostructure substrate exhibits a much better SERS activity (figure S7, supporting information). A molecular concentration as low as 10^{-8} M can be detected from the superhydrophobic substrate, which is 10^3 times lower than the pristine one can afford. Furthermore, the SERS activity can be improved as well upon deposition of metal nanoparticles. (figure S7(c), supporting information). These results clearly show the generality of the SERS substrates we proposed. On the other hand, the SERS activities of the hierarchical nanostructures have been also evaluated with 785 nm laser excitation (figure S8, supporting information). The results clearly indicate that the superhydrophobic silicon hierarchical nanostructure substrate preserved the superior SERS activity in comparison with that of the pristine one. In addition, introducing metal nanoparticles could also improve the SERS activity of the substrate, which was similar to the situation with the 532 nm excitation.

The above results clearly demonstrate the feasibility of employing superhydrophobicity to improve the SERS performance of dielectric silicon nanostructures. To demonstrate its real-life applications, the hybrid superhydrophobic silicon substrate was utilized for food safety monitoring. To that end, commercial milk mixed with melamine of a specific concentration was added to the hybrid substrate. Before the Raman measurement, the milk was purified by removing most of the protein to suppress the strong background signal.
Subsequently, 10 μl of the resulting pale-yellow purified solution was drop-casted onto the hybrid superhydrophobic substrate for SERS characterizations. As shown in figure 7(c), for the milk without the melamine molecules, no characteristic Raman band could be collected from the hybrid silicon nanostructure substrate. In contrast, a well-resolved Raman band at 677 cm⁻¹, which corresponded to the ring-breathing mode II of the melamine, was observed in milk treated with 10⁻⁵ M melamine. Such a concentration fulfills the requirement set by the Codex Alimentarius Commission for powder infant formula (2.5 mg L⁻¹: 2 × 10⁻⁵ M) [38]. These results unveil the potential of the hybrid superhydrophobic silicon substrate for tracing food toxins in our daily lives. One should note that several spectral features could be observed in addition to the 677 cm⁻¹ mode from both of the spectra shown in figure 7(c). We believe that they originated from the small quantity of protein residue in the purified milk.

4. Conclusions

In summary, we have proposed a facile approach to improve the performance of the dielectric SERS substrate. By functionalizing hierarchical silicon nanostructures with PFOT, the nanostructure can be modified into a superhydrophobic surface. Such a surface can be utilized to concentrate the molecule droplet into a small area. The detection limit of the SERS substrate can therefore be lowered to be smaller than 10⁻⁸ M, which is the best result ever reported in pure dielectric SERS substrates. Furthermore, SERS capability can be improved by depositing gold nanoparticles onto the superhydrophobic hierarchical silicon nanostructures, whereby the detection limit can be as low as 10⁻¹¹ M. As a simple demonstration of its real-life applications, we showed that a superhydrophobic substrate deposited with gold nanoparticles could be employed to detect melamine molecules in liquid milk, where a concentration of 10⁻⁵ M could be traced. Our strategy was to strongly promote dielectric nanostructures as an excellent SERS substrate and therefore pave the way for the fabrication of low-cost sensors with ultrahigh sensitivity, which could be widely used in food-safety inspection and environmental monitoring.

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ORCID iDs

Huanjun Chen https://orcid.org/0000-0003-4699-009X

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