

MOLECULAR SENSING BY SERS USING ENTANGLED NANOFIBERS

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1 INTRODUCTION

1.1 RAMAN SPECTROSCOPY

Spectroscopy is the use of light-matter interaction to characterize inherent properties of materials. The unique interaction of light with materials results in absorption or scattering that varies in strength across wavelengths. The resultant relation between the intensity and wavelength of the scattered light is called a spectrum and is characteristic of certain materials or class of materials. Because light interacts with matter through absorption, refraction, emission, and scattering, different types of spectroscopy rely on

the type of light-matter interaction that takes place. For instance, Raman spectroscopy relies on the inelastic scattering of light. The types of scattering are represented in Fig. 1.

Elastic scattering, also known as Rayleigh scattering, occurs when there is no energy transfer and the scattered energy (E_s) is equal to the incident energy (E_0). Inelastic scattering occurs when energy transfer follows a scattering between incident irradiation and material, manifested by E_s distinct from E_0 . Inelastic scattering is categorized into two: Stokes scattering—if the resultant E_s is smaller than E_0 —and anti-Stokes scattering, if E_s is larger than E_0 . Occurrence of Stokes scattering dictates that an energy state is excited from a ground state, meaning that it is much more likely to occur at room temperature than anti-Stokes scattering that is common at elevated temperatures because of the prerequisite of excited states. The difference between the incident (E_0) and outgoing energy (E_s) is referred to as a “Raman shift” and reliant on vibrational modes of the molecule. A Raman shift is expressed in wave numbers (ω) as follows:

$$\Delta\omega \text{ (cm}^{-1}\text{)} = \left\{ \frac{1}{\lambda_0 \text{ (nm)}} - \frac{1}{\lambda_s \text{ (nm)}} \right\} \times 10^7 \frac{\text{(nm)}}{\text{(cm)}}, \quad (1)$$

where $\Delta\omega$, λ_0 , and λ_s are the Raman shift, the incident wavelength, and the scattered wavelength, respectively.

For an inelastic scattering, for example, Raman scattering, to occur, a bond motion (stretch, wag, etc.) must change the polarizability of the molecule. Polarizability is defined as the ease of distortion of the electronic cloud in the presence of an electric field or, in layman’s terms, how loosely the electron cloud is bound to the molecule. In linear molecules, such as CO_2 ($\text{O}=\text{C}=\text{O}$), infrared (IR) and Raman modes are mutually exclusive. Modes that change the polarizability such as the symmetrical stretch mode are Raman-active, and those that alter the dipole moment are IR-active. Fig. 2 shows the single Raman-active mode of CO_2 and the two IR-active modes.

Note that the Raman-active mode changes the distance of the oxygen atoms from the carbon atom. They are either both closer together or both farther apart to alter the polarizability of the molecule. The IR-active mode also changes carbon–oxygen distances, but in this case, the changes cancel out. The strength of Raman peaks is correlated to the change in polarizability caused by the corresponding mode. Molecules such as H_2O have Raman-active modes that are very weak because the change in polarizability caused by change in relative $\text{O}=\text{H}$ distance is very small.

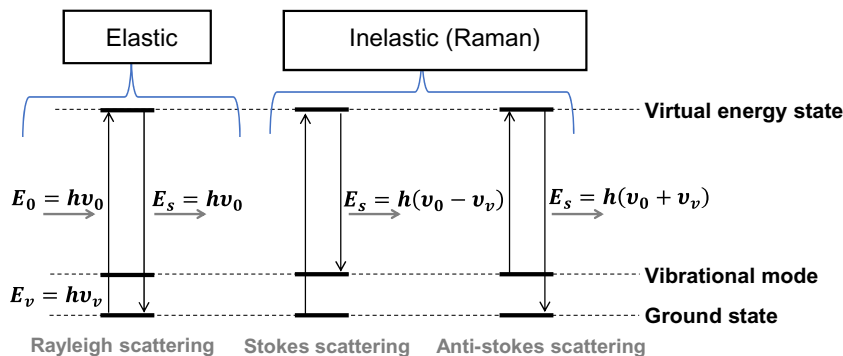


FIG. 1

Representation of various types of scattering.

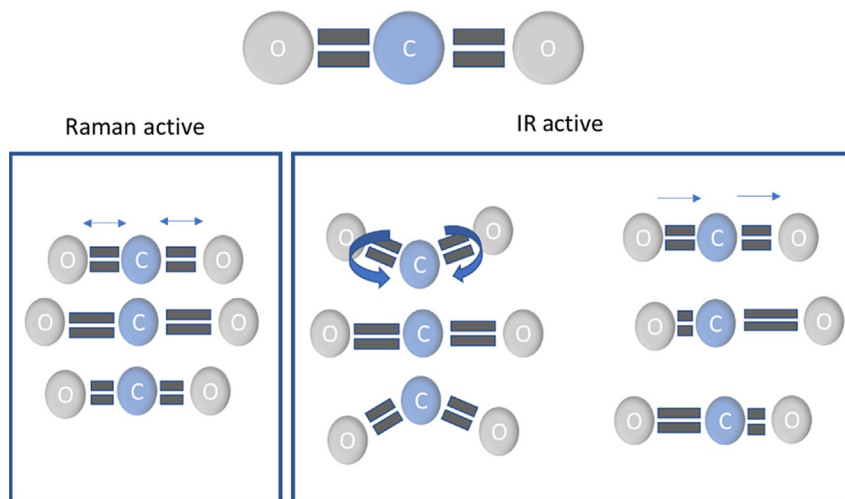


FIG. 2

Illustration of the spectrally active modes of carbon dioxide.

The strength of the Raman peak also depends on the intensity of the incident beam:

$$P_s(\nu_s) = N\sigma_{RS}I(\nu_i) \quad (2)$$

where $P_s(\nu_s)$ is the power of the Raman scattered photons, N is the total number of scatterers in the laser focal volume, σ_{RS} is the Raman scattering cross section, and $I(\nu_i)$ is the intensity of the incident light. Even for chemical species with strong Raman-active vibrational modes, the Raman scattering cross section is very small, ascribed to the large difference in the energy of the irradiating photon and the molecular vibrational modes. The size of the Raman scattering cross section is estimated on average to be $\sim 10^{-30}$ cm²/molecule. As a general comparison, a Raman scattering cross section in the unit of squared centimeter per molecule is about 10 order of magnitude smaller than the fluorescence cross section of common fluorescent species [1]. The limitation in the scattering cross section has confined the application of Raman spectroscopy to materials at a bulk or highly concentrated state.

Despite the limitation of low scattering cross section, Raman spectra are still an invaluable tool for scientists. The sharp peaks produced by the inelastic scattering do not overlap nearby vibrational modes, producing a specific and easily distinguishable fingerprint for chemical species. The lack of a broad –OH peak as often seen in IR spectroscopy also indicates that Raman spectroscopy may be more easily applied in aqueous solutions and biological systems. Raman spectra can be taken without contacting the sample, making it a nondestructive technique. Acquisition time can be as low as milliseconds, and the basic components of a spectrometer, a laser, CCD detector, and microscopes are easy to obtain and miniaturize, adding versatility to this technique. On-chip Raman systems have already been reported in the literature [2, 3]. Improving the sensitivity of Raman spectroscopy would allow researchers and industrial users to fully utilize this technique and contribute significantly to the analysis, detection, and monitoring of various chemical and material systems.

1.2 SURFACE ENHANCED RAMAN SPECTROSCOPY

The field of Raman spectroscopy has seen a paradigm shift in 1974 when Martin Fleischmann reported his observation of enhanced Raman signal from pyridine adsorbed on a roughened Ag surface [4]. Though he was not able to explain the mechanism at that time, his discovery would lead to the creation of the field of “surface-enhanced Raman spectroscopy” or simply SERS.

After Fleischmann’s report, several groups tried to explain the phenomena he observed. In 1977, Albrecht et al. proposed a charge transfer mechanism [5]. In the same year, Van Duyne has proposed a theory based on electromagnetic (EM) enhancement [6]. Since these initial reports, the community of SERS researchers has largely agreed that there are two contributions to the enhancement of Raman signals of molecules adsorbed onto metal surfaces. “Chemical enhancement” is defined as the enhancement related to the charge transfer that requires chemical bonding between molecule and surface [5, 7]. The enhancement arising from the local interactions of the incoming radiation and the surface plasmons on the metal surface is commonly called “electromagnetic enhancement.”

The power of the SERS signal is proportional to the multiplication of the square power of both the incident and the scattered fields, as follows:

$$P_s(\nu_s) = N\sigma_{\text{SERS}}L(\nu_s)^2L(\nu_i)^2I(\nu_i) \quad (3)$$

The enhancement of the fields can be described by the following formula where $|E_{\text{loc}}(\nu)|$ represents the amplitude of the enhanced electric field:

$$L(\nu) = \frac{|E_{\text{loc}}(\nu)|}{|E_0|} \quad (4)$$

When the incident and scattered light are similar in frequency, we can assume that both the incident and scattered fields are enhanced equally. The EM-SERS enhancement can then be approximated as the fourth power of the enhancement of the incident field, which is a function of the interaction between the incoming light and the surface plasmon on the metal. The exact scaling of the chemical enhancement still remains to be clarified, but it is approximated as a square of the Raman cross section [1].

Twenty years after Albrecht and Van Duyne first proposed the mechanisms for SERS enhancement, Kneipp et al. [8] and Nie and Emry [9] reported the detection of a single molecule via SERS with an estimated enhancement of 10^{14} . The development of SERS substrates to improve and eventually maximize the enhancement factor has been a subject of many research papers and years of development. These efforts can be grouped into three general strategies for maximizing the field enhancement: (i) packing electric field lines at sharp tips [10–28], (ii) coupling near fields at narrow gaps [29–57], and (iii) resonating the surface plasmons [58–71]. The first two strategies may or may not involve plasmonic resonance, but the third strategy demands a plasmon-resonant substrate, generally a periodic array of well-defined plasmonic features.

The most popular strategy is to manufacture a plasmon-resonant substrate [58–72]. By matching the resonance of the substrate with the Raman excitation, it is possible to maximize the near-field enhancement. However, when the difference in frequencies of the scattered and incident fields is large, structures that rely on resonance with a given wavelength may not effectively enhance at all the available wave numbers [73–75]. For resonant SERS substrates, it has been shown that the optimal excitation is one that is blueshifted with respect to the local surface plasmon resonance of the substrate [76]. This optimizes the enhancement across a broadband of frequencies at the cost of the strongest possible enhancement at the resonance peak. We argue that a nonresonant substrate that can give high field enhancement is the optimal SERS substrate.

1.3 KISSING NANOFIBER JUNCTION BASED SERS SUBSTRATES

Since the demonstration of the single-molecule detection via SERS in 1997, much research has focused on the understanding of the mechanism of SERS-based chemical detection and the development of high-performance SERS substrates [9, 77]. As discussed in the previous section, the most popular class of substrates are plasmon resonance-based substrates. These substrates generally consist of arrays of nanometer-sized gaps between metal structures. In the previous section, we discussed the difficulty of optimizing these substrates for a wide range of frequency bands. In addition to this failing, the spatial uniformity of the enhancement of these substrates depends entirely on proper fabrication technology. A slight tolerance, on the order of magnitude of a few nanometers in fabrication, can move the resonance frequency by tens of nanometers [41, 55, 78], hampering the degree of field enhancement. Given these limitations, desirable is a substrate with broadband enhancement and thus less reliant on tight geometric tolerances. One such substrate architecture is plasmonic kissing junctions.

Plasmonic kissing structures create the EM enhancement by concentrating the electromagnetic energy around the junctions by the adiabatic compression of the surface plasmons. This class of structures can provide electric field enhancements of more than three orders of magnitude, which is the accepted limit for single-molecule detection [1, 79–82]. Modeling the exact enhancement of arrays of plasmonic kissing junctions is a complex problem, for which reason, a thorough, substrate-level modeling has not yet been carried out. However, one can find detailed information on the plasmonics of a single finite nanowire [83–85] and some special configurations of nanowire dimers [86–88]. When such nanowires are brought together close enough, they can act as a single plasmonic body that carries hybrid modes in itself. The energy of the hybrid modes depends on the relative orientation of the individual dipole (or multipole) moments, the distance between the axes and the symmetrical conditions [86–88].

Producing the kissing-nanofiber-junction-based SERS substrates can be achieved in many ways. Bottom-up, nonlithographic techniques such as nanowire array construction can provide great enhancement at little fabrication cost [89–91].

1.4 OUTLINE AND GOAL OF THIS CHAPTER

In this first section, we review the basics of Raman spectroscopy and SERS and introduce the concept of kissing nanofiber junctions as an effective building block for SERS substrates. In the remainder of this chapter, we share our story of establishing a nanomanufacturing method to embody the kissing nanofiber junctions and of applying thus prepared SERS substrates to the detection of multiple chemical species in a mixture. In the course of the multiple species detection, we characterize a competitive adsorption phenomenon.

2 CNT FORESTS FORMS A SCAFFOLD OF NUMEROUS KISSING NANOFIBER JUNCTIONS FOR SERS SUBSTRATE¹

In this section, we report the design and development of a highly sensitive substrate for surface-enhanced Raman spectroscopy (SERS) enabled by arrays of Au-coated metallic carbon nanotubes (CNTs) having a high-k dielectric (hafnia, HfO₂) nanolayer insert as a potential barrier. Repeated

¹This section is adapted from A. O. Altun, S. K. Youn; N. Yazdani; T. Bond; H. G. Park., Metal-dielectric-CNT nanowires for femtomolar chemical detection by surface enhanced Raman spectroscopy, *Adv. Mater.* 25 (2013) 4431–4436.

demonstration of femtomolar detection of 1,2-bis(4-pyridyl)ethylene (BPE) in the solution phase is performed with the nonresonant substrate. Comparison of SERS performance with and without the hafnia potential barrier establishes the critical contribution of this dielectric nanospacer to the enhanced sensitivity. This finding is attributed to the relief of plasmon leakage in the presence of the virtual energy potential barrier. CNTs, when covered by dielectric barriers, can be a valuable template for constructing a metal-dielectric-CNT nanowire structure for a practical and reproducible SERS substrate.

2.1 RATIONAL DESIGN OF THE SUBSTRATE

Here, we present a rational design of a SERS substrate based on a metal-dielectric-CNT fiber structure and demonstrate femtomolar-level detection sensitivity. By inserting a nanometer-thick layer of hafnia between Au and CNT and random stacking of these Au-hafnia-CNT nanowires, we were able to enhance the SERS detection performance considerably, demonstrated by femtomolar detection of BPE. In the next sections, we discuss rational design, fabrication procedures, plasmon properties characterization, and the SERS performances of the Au-hafnia-CNT nanowire array samples. We also investigate the effects of the thickness of hafnia and Au layers in order to define the optimized geometry and material conditions for maximum SERS detection sensitivity.

An important part of our paper is devoted to the experimental evidence of the contribution to the SERS signal by a dielectric barrier in between CNT and noble metal. As depicted in Fig. 3, the work functions of multiwalled CNT and Au are about 4.95 [92] and 5.1 eV, respectively, with small Coulomb blockade. Such a small potential difference may not be able to prevent direct electron transfer between Au and CNT. This electron transport interaction may result in quenching of localized surface plasmons on the Au surface. An insertion of high- k , large bandgap dielectric material such as hafnia could temper this quenching mechanism, thereby leading to a higher field enhancement on the surface of the metal nanostructure. It has already been reported that the fluorescence of dye molecules is quenched when they are attached on CNTs due to an electron transfer between the excited states of the dye molecule and low-lying energy states of CNT [93]. Likewise, photoluminescence intensity and lifetime of quantum dots (or rods) can considerably decrease upon conjugation with CNT [94] or amorphous carbon film [95], attributed to a Förster resonance energy transfer. Furthermore, in another study by

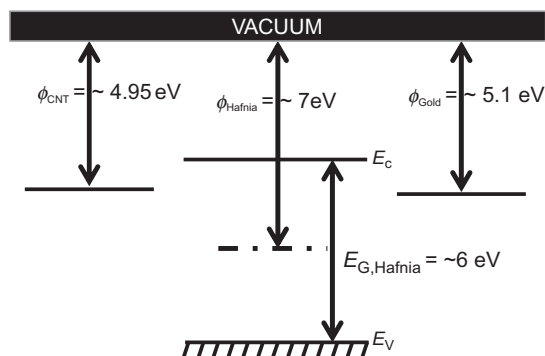
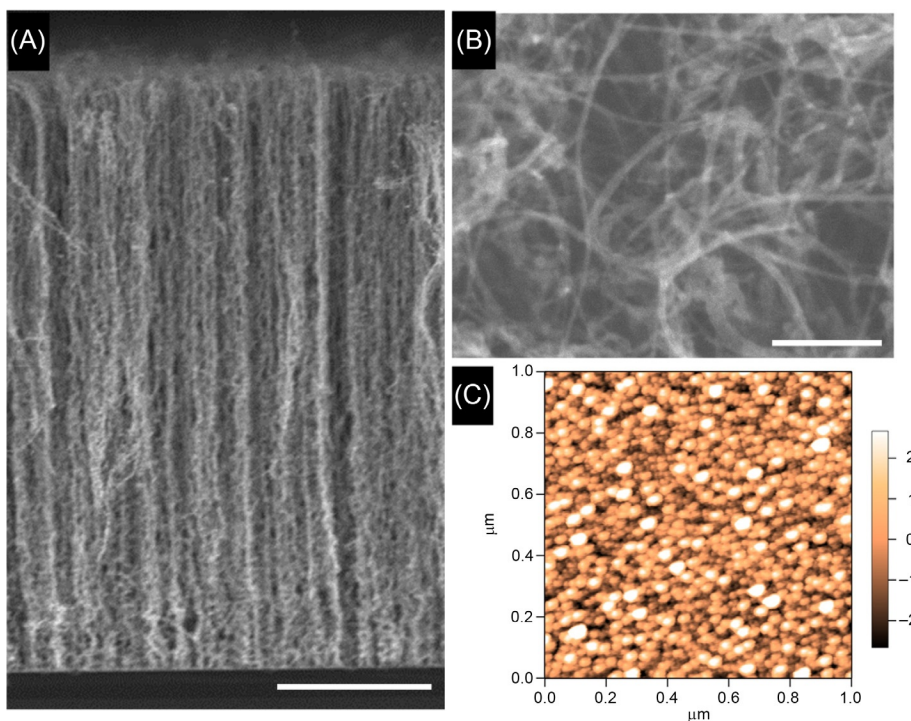


FIG. 3

Band diagram of multiwalled CNT, hafnia, and Au. ϕ , work functions. E_G , bandgap.

**FIG. 4**

SEM images of the synthesized VA-CNT forest along with the AFM image of the deposited catalyst. (A) Cross-sectional SEM image of the VA-CNT forest (scale bar: 10 μm). (B) Top view of VA-CNT forest (scale bar: 100 nm). (C) AFM image of the catalyst deposited for the VA-CNT growth (scan area: 1 $\times$ 1 μm).

Sanles-Sobrido [96], the resonance peak of Ag nanoparticles disappeared when contacted to CNT, suggesting that the surface plasmon properties could indeed be influenced by CNT. Therefore, we introduced atomic layer deposition (ALD) of hafnia on CNT samples prior to the Au evaporation. Hafnia in particular was selected due to its high dielectric constant and bandgap ($\epsilon_r = 25$ and $E_G = 6\text{ eV}$). In our design, vertically aligned carbon nanotube (VA-CNT) substrates will be conformally coated with hafnia of various thicknesses and then coated with Au of various thicknesses in order to optimize the SERS effect created by the CNT array template via suppression of plasmon leakage. With this rational design, our goal is to achieve enhanced sensitivity of SERS molecular detection in a liquid cell configuration (Fig. 4).

2.2 FABRICATION OF THE SUBSTRATE

VA-CNT samples were prepared by chemical vapor deposition (CVD) using catalysts of 1-nm-thick iron atop 20-nm-thick Al on 1 $\times$ 1 cm^2 silicon substrates. The film was then annealed in a cold-wall CVD furnace (Black MagicTM, Aixtron) at a temperature of 750°C for 10 min. The average areal

number density of catalyst islands, approximately equivalent to the average areal number density of CNTs, measures $500\mu\text{m}^{-2}$ by atomic force microscopy.

For the CVD process, the catalyst substrate was loaded into the same CVD furnace followed by chamber evacuation below 0.2 mbar. The reactor temperature was held above 100°C during loading/unloading to minimize moisture condensation. Under a shower head gas flow of hydrogen (200 sccm) and argon (300 sccm), the reactor temperature was raised to the growth temperature (750°C) at a ramp rate of $300^\circ\text{C}/\text{min}$ and maintained there for 5 min for catalyst reduction, while the total chamber pressure was kept at around 6–7 mbar. During the CNT growth step, 5 sccm of acetylene was added for 15 min at 480 mbar total pressure. Upon completion of the growth step, the reactor was cooled down in argon. A uniform and dense forest of VA-CNT was synthesized as a mixture of multi- and few-walled nanotubes from the existence of the radial breathing mode (RBM) peaks in the Raman spectra. The length of CNTs is about $40\mu\text{m}$. The diameters of as-synthesized CNTs are $8.8 \pm 0.7\text{ nm}$. Most of the tips of CNTs were bent.

Conformal coating of CNT by hafnia was performed by ALD (Picosun Sunale). One single cycle of an ALD is composed of 1 s pulse of tetrakis(ethylmethyamido)hafnium (TEMAH) and successive 1 s pulse of water vapor followed by a nitrogen purge of 7 s, all performed at a substrate temperature of 300°C that is much below our CNT substrate can withstand without degradation. Three different thicknesses of hafnia were deposited using 30, 60, and 90 cycles. On the hafnia-coated CNT arrays, Au was deposited by e-beam evaporation. Average thickness of the deposited Au film on the CNT-hafnia nanowires was measured by SEM (Fig. 5).

2.3 DEMONSTRATION OF THE FEMTOMOLAR SENSITIVITY

All Raman and SERS measurements were carried out using a 785 nm Raman system (Nuscope™, Del-tanu), with a beam power of 5 mW and integration time of 5 s. The SERS performance of the substrates was tested using BPE (Sigma-Aldrich, >99.9%) in a liquid cell. In order to obtain an average value of the SERS intensities, 20 measurements were made focusing at different point for each of the concentrations. The typical substrate size used in the experiments was 4 mm^2 , and the total volume of the BPE solution in the liquid cell setup was $150\mu\text{L}$. The depth of focus and the diameter of the focal spot of the Raman laser are 70 and $35\mu\text{m}$, respectively. A 13-mM BPE solution was made by dissolving BPE powders (17 mg) in methanol (7 mL) at room temperature and sonicating for 3 min. This solution (1 mL) was then diluted with methanol (25 mL), process of which continued for successive dilution. In the liquid cell, the SERS substrate was placed, and the BPE solution of a known concentration was added. The SERS signal was obtained by focusing the laser beam on the CNT surface through the liquid solution, followed by repeated measurements on several spots. In obtaining the SERS spectra of BPE, baseline correction was made by subtracting the background spectrum of the methanol (Fig. 6) using the five-step algorithm of the built-in software of the Raman system.

The procedure of substrate preparation and molecular detection are two important aspects of SERS. SERS data of species can be taken either in solution or in a dry environment. In the solution-based SERS characterization, the Raman laser is focused on the substrate immersed in a solution that contains a known concentration of species to probe, and the SERS hot spots are frequently visited by the species under Brownian motion. In the dry measurements, on the other hand, SERS signals are obtained on the substrate after it is incubated in the solution and dried completely. It should be noted that the drying procedure could cause a nonuniform stacking of the analytes over the substrate surface, resulting

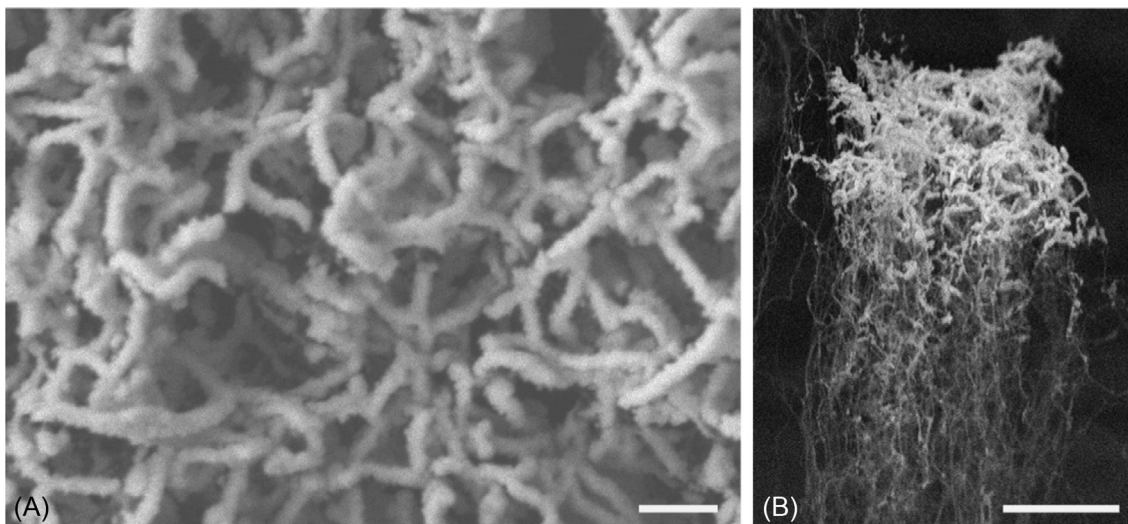
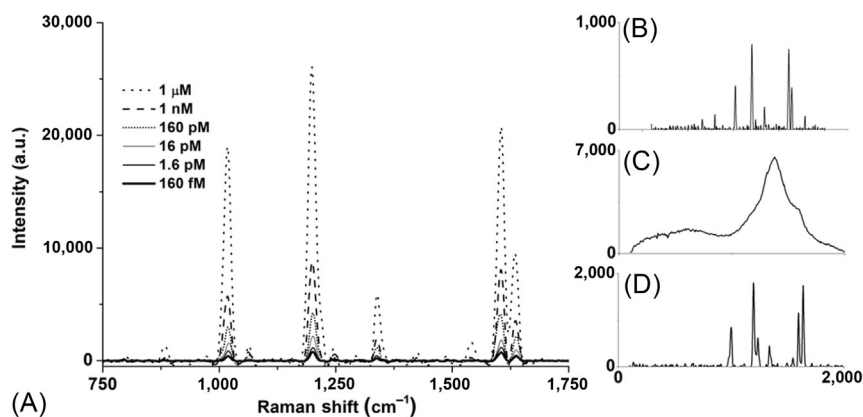


FIG. 5

(A) SEM image of VA-CNTs coated with 2.5-nm-thick hafnia and 21-nm-thick Au (scale bar: 200 nm). (B) A bundle of the Au-hafnia-CNT sample (scale bar: 1 μm).

**FIG. 6**

(A) SERS of BPE solutions in various concentrations, (B) SERS of a 160 fM BPE solution, (C) background SERS of methanol, and (D) Raman spectrum of 1 M BPE.

undesirably in preferential coating on the SERS hot spot regions [97] consequently hampering a correct characterization of the substrate. Therefore, results of low detection limits by the use of the dry measurement cannot necessarily warrant that the same substrate will show as high detection sensitivity in a wet measurement. In addition, the substrate needs to be validated in solution in order to claim that a SERS substrate is useful for field applications as a molecular sensor. Therefore, employing BPE as a test species, all our SERS measurements were made in the wet environment of a liquid cell.

Our metal-dielectric-CNT substrates enabled femtomolar detection sensitivity in the wet SERS measurements (Fig. 6). Among the characteristic peaks of BPE at around 1010, 1200, 1610, and 1640 cm^{-1} , we opted for 1200 cm^{-1} for characterizing the concentration dependence of our SERS substrate. This peak corresponds to ethylenic C=C stretching mode [98–100]. Fig. 7 shows the concentration-dependent Raman intensity of our CNT-templated Au nanowire substrates with and without the hafnia insert. A dramatic enhancement of detection limit by five orders of magnitude in molar concentration was observed in the presence of the hafnia barrier. We believe that this high SERS sensitivity originates from the top few-micrometer part of the hafnia-CNT forest penetrated by Au physical vapor deposition, illustrated in Fig. 5. Since the very top part of our VA-CNT sample has a canopy of bent nanotubes, the resultant structure resembles horizontally or obliquely stacked Au-hafnia-CNT nanowires. Since the expected role of CNT in our design is only a template for the Au nanowire formation, the CNTs' undesirable action as an electron sink should be prevented by the use of the high- k dielectric (hafnia) insert. Indeed, when Au was directly deposited on the VA-CNT forest without any dielectric barrier, we could observe SERS signal merely above the nanomolar level (Fig. 7).

We attribute this strong SERS signal and femtomolar-sensitive detection to the abundance of the Au-hafnia-CNT nanowire junctions per unit area. Some of these junctions can apparently result in strong hot spots as suggested by the previous studies [80, 81, 91, 97, 101]. In combination with the elimination effect of plasmon quenching by a high- k dielectric barrier, these nanowire junctions could manifest their use in highly sensitive SERS measurements. Interestingly, the aforementioned sensitive SERS performance was achieved without a visible plasmon resonance in the far field. This absence of

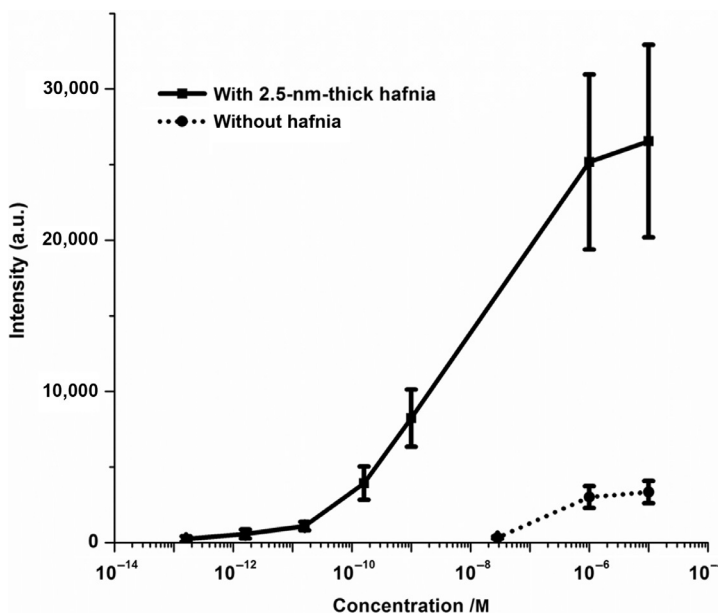


FIG. 7

SERS intensity at 1200cm^{-1} of the 21-nm-thick Au-coated VA-CNT samples with and without hafnia.

neat and isolated plasmon resonance is perhaps due to the random configuration and distribution of Au nanowire junctions and thus resonances, at the canopy of our substrate. Accordingly, our study proves that it is possible to produce a SERS substrate that is cheap, uniform, and repeatable; requires no lithographic techniques; and can facilitate strong hot spots even without a requirement of far-field plasmon resonance.

2.4 SECTION CONCLUSIONS

In conclusion, we designed a metal-dielectric-CNT nanowire structure; fabricated reproducible, high-performance SERS substrates without conspicuous far-field plasmon resonance; and demonstrated femtomolar detection of BPE on these substrates. In this design, CNTs provide a template for the formation of Au nanofibers, and we postulate that hafnia has a double role: (i) as a high- k dielectric barrier in between Au and CNT, it can sustain Au surface plasmons by preventing a coupling between electron energy levels of Au and CNT and (ii) also induces bunching of the nanowires and thus the generation of a wider number of hot spots. Numerous random junctions among these Au-hafnia-CNT composite nanofibers can create SERS hot spots necessary for noninvasive molecular detection. Therefore, it is the combined effect of surface plasmon shielding and “kissing nanofibers” [80, 81, 91, 97, 101, 102] that is responsible for the enhanced molar detection limit by more than five orders of magnitude in comparison with simple Au-on-CNT structures. Further theoretical and experimental studies are necessary to unveil the detailed effects of geometric variation and energy-coupling shielding on the SERS sensing of various species.

3 APPLICATION: SENSITIVE DETECTION OF COMPETITIVE MOLECULAR ADSORPTION BY SERS²

In this section, we illustrate an application of SERS as an effective analysis tool of surface adsorption phenomena. Surface adsorption plays a critical role in a wide variety of fields from surface catalysis to molecular separation. Despite the importance, limited access to simultaneously sensitive and selective detection mechanisms has hampered the acquisition of comprehensive and versatile experimental data needed to understand the complex aspects of mixture adsorption, calling for a molecular detection method capable of obtaining the surface adsorption isotherms over a wide range of concentrations and distinguishing the competitive adsorption of different adsorbates.

3.1 RATIONALE AND OBJECTIVES

Understanding the surface adsorption phenomenon has been one of the main issues of physical chemistry for decades. Surface catalysis, etching, corrosion, separation, chemical vapor deposition, and electrodeposition can be designed more rationally with a better knowledge of the surface adsorption physics. Methods for determining adsorption isotherms rely prevalently on volumetry [103, 104], gravimetry [103–105], voltammetry [103], and calorimetry [106–108], most of which bear a certain extent of technical challenges in detecting a trace amount of chemicals at the surface. For instance, most adsorption isotherms found in the literature based on these methods show as low a detection limit as nanomolar. Also, the absence of selective sensing mechanisms could dwindle the distinguishability of individual isotherms amid simultaneous adsorption of multiple chemical species on a surface. These challenges call for a sensitive and selective sensing technique capable of facile recognition of chemical adsorbates over a wide range of concentrations amid competitive adsorption.

SERS is a selective and rapid molecular detection method based on the orders of magnitude amplification of the molecule-specific spectral signals via metallic nanostructures [4, 9, 109]. The amplification of the SERS signal is proportional to the fourth power of the electric field enhancement induced by the coupling of surface plasmons of metallic nanostructures with the light [9, 109]. Various nanoarchitectures and micro-nanomanufacturing techniques have been utilized to realize a strong SERS enhancement eventually demonstrating subpicomolar detection of various analytes [9, 39, 44, 78, 109–114]. Besides the sensitivity, SERS is a selective technique, for it provides a fingerprint spectrum of chemical species.

It has been widely accepted that the SERS signal intensity is reliant on the local chemical concentration within the hot spots (locations of enhanced electric field) of the SERS substrate. Assuming that the number of molecules inside the hot spots is linearly proportional to the total number of the molecules adsorbed on the surface, SERS can be used to obtain the surface adsorption isotherms. Indeed, researchers have utilized SERS to characterize the surface adsorption isotherms [110, 111, 115–126]. Langmuir [115–124], Freundlich [111, 124, 125], and Brunauer–Emmett–Teller (BET) [126] models are often utilized to relate the SERS data and isotherms. An ultrasensitive SERS substrate can show a

²This section is adapted from A. O. Altun, Multiscale Plasmonics for Energy and Environment (PhD Thesis), ETH Zurich, 2014; and also adapted with permission from A. O. Altun, T. Bond, W. Pronk, H. G. Park, Sensitive detection of competitive molecular adsorption by surface-enhanced Raman spectroscopy, *Langmuir* 33 (2017), 6999–7006. Copyright 2017 American Chemical Society.

larger picture of the surface adsorption isotherms as it can detect the surface coverage at ultralow concentrations. Such comprehensive data would facilitate a more realistic physical modeling of the adsorption process.

Although the sensitivity of a SERS substrate is generally described by its ability to enhance the electric near field, the amplification of the SERS signal depends also on the interaction between the chemical species and the substrate surface. The chemical species having strong affinity to the metallic surface have a higher chance to fill the hot spots, leading to stronger SERS signals. This effect is particularly important for the solutions of multiple constituents in which molecules of each species have their own affinity to the substrate because analysis of a complex mixture becomes a key capability for such applications as pesticide detection and micropollutant monitoring. In this context, the first important question is how to detect a compound amid competitive adsorption with others to a SERS substrate. The next question is the possibility of estimating the competitive adsorption isotherms, given the single-compound isotherms? To answer these questions, it is crucial to undergo systematic SERS characterization of a chemical mixture having various binding energies.

In the previous section, we have successfully established a facile preparation method of a high-performance SERS platform, out of a myriad of plasmonic nanowires intertwined to one another [110]. This platform enables femtomolar-level detection of a test organic species, BPE. By the use of this ultrasensitive platform (Fig. 8A), here, we characterize the surface adsorption of three different species and their binary mixtures. We choose two strongly binding species, that is, BPE and benzo-triazole (BTAH), and a weakly binding species, that is, ibuprofen (Ibu). Ibu is a popular pharmaceutical for pain relief and BTAH a well-known corrosion inhibitor (Fig. 8B). These chemicals are two micropollutants of a growing concern in the water resources that threaten the biodiversity and human health [127, 128]. Thus, early detection of these micropollutants at trace concentration can critically avail the environmental monitoring. Through this characterization, we aim to understand competitive adsorption

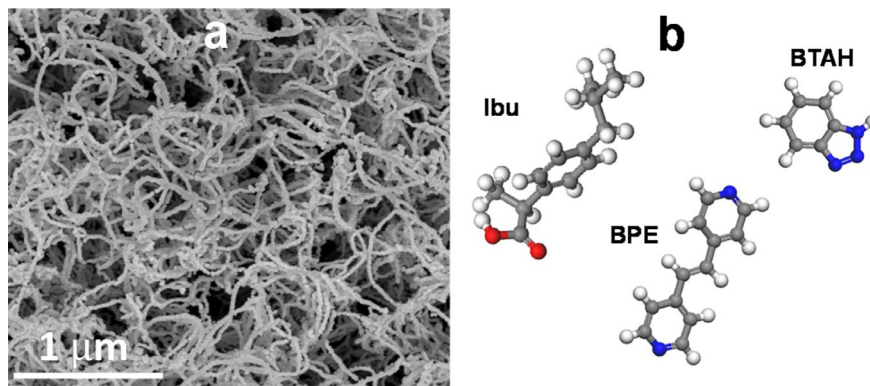


FIG. 8

(A) Scanning electron microscope (SEM) image of the Ag-HfO₂-CNT (carbon nanotube) substrate used in the experiments. (B) Schematic illustration of molecules used in the SERS characterization: Ibuprofen (Ibu), BTAH, and BPE. Red, white, gray, and blue symbols represent oxygen, hydrogen, carbon, and nitrogen atoms, respectively. For color interpretation see online.

isotherms of chemical species with different binding affinities to the substrate surface while exploring the potential of the SERS technology for multicomponent micropollutant detection.

The first part of this section presents results of the concentration-dependent SERS measurements for the single-compound solutions. We will calculate binding energies to Ag along with minimum-energy configurations of molecules to interpret the SERS data. In the second part, we will present the experimental results of the competitive adsorption isotherms of the multiple-compound solutions. We will try to implement the generalized Langmuir isotherm by fitting both the single and multicomponent solutions.

3.2 EXPERIMENTAL AND METHODOLOGY

3.2.1 Molecular dynamics simulations

We used the FORCITE module of Materials Studio 6.0 (Accelrys Inc., San Diego, USA) to perform the geometry optimization and molecular dynamics simulations. Simulation cells were formed and relaxed before forming a 3D periodic box of 350 methanol atoms with one target molecule. Geometry optimization was performed on this cell prior to placing it on the Ag [111] surface. If necessary, additional geometry optimization was performed after the placement of the adsorbent molecule in the vicinity of the surface. Molecular dynamics simulation was performed by the use of the isochoric, isothermal (NVT) ensemble. Total simulation time, time step, and the reconfiguration interval of the simulations were 400 ps, 1, and 1000 fs, respectively. The temperature was set to 300 K. The simulation employed COMPASS [129] force field that combines bonded and nonbonded force components.

In order to calculate the binding energies, three additional simulations were implemented considering (a) adsorbate and methanol, (b) methanol and Ag, and (c) only methanol. The binding energy for each case was calculated according to the following formula [130]. The resultant binding energy values are reported as an average of the three simulations. Values of standard deviation are smaller than 10% in our calculation:

$$E_b = E_{\text{total}} + E_{\text{MeOH}} - E_{\text{adsorbate} + \text{MeOH}} - E_{\text{MeOH} + \text{Ag}} \quad (5)$$

3.3 RESULTS AND DISCUSSIONS

3.3.1 Adsorption of single-compounds

Our SERS substrate enables the detection of BPE and BTAH, micropollutant surrogates of this study, down to 200 and 500 fM concentrations, respectively, confirming the previously reported femtomolar sensitivity [110]. The characteristic bands of the spectra shown in Fig. 9A and B agree with the reported SERS spectra of these species [97, 110, 131]. From numerous experiments carried out with various CNT growth conditions and thicknesses, we rediscover that the substrates having a shape of intertwined metal nanowire canopy (Fig. 8A) can yield strong SERS signals. The CNT forest density is an important parameter. A dense CNT forest results in more nanowire junctions per unit projection area, allowing higher field enhancement and stronger SERS signal. However, if the CNT forest is too dense, metal would not coat nanowires individually but rather blanket the entire CNT canopy to form rough, continuously porous texture leading to diminution of the SERS signal. HfO_2 intermediary plays a role of a dielectric barrier to eliminate the Ag surface plasmon quenching by CNT [110], while an excess coating of HfO_2 could aggregate nanowires to negate eventually local electromagnetic field enhancement.

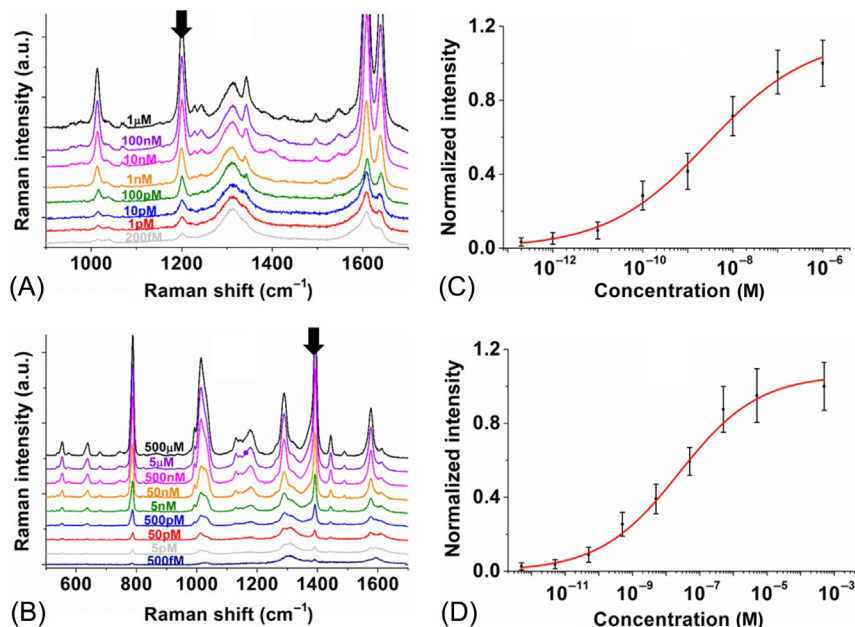


FIG. 9

SERS spectra of (A) BPE and (B) BTAH at various concentrations. Concentration-dependent SERS intensities of (C) BPE and (D) BTAH, respectively. Detection limits are 200 and 500 fM for BPE and BTAH, respectively. The concentration-dependent SERS signals are plotted using the intensities of the bands at 1200 and 1392 cm^{-1} (indicated by a black arrow) for BPE and BTAH, respectively. Generalized Langmuir model predictions are shown on the concentration-dependent SERS signals of BPE and BTA.

Hence, there are optimum thicknesses of Ag and HfO_2 to create a canopy of intertwined nanowires full of Ag “kissing nanowire” junctions.

Regarding concentration-dependent SERS intensities, our sensitive substrate allows to obtain adsorption isotherms by detecting the analytes in the femtomolar-to-micromolar concentration range. We select bands at 1200 and 1392 cm^{-1} from the SERS spectra of BPE and BTAH, respectively (Fig. 9C and D). It is remarkable that both intensity-concentration diagrams show a sigmoidal curve in a linear-log plot, in excellent agreement with our previous results [110].

Since BPE and BTAH are known to chemisorb on the metallic surfaces [97, 131, 132], the subpicomolar detection limits can be explained partly by their strong affinity, if not entirely by the strong electromagnetic field enhancement of the kissing nanowires. Our substrate demonstrated a poorer detection limit (500 nM) for Ibu that does not bind to the metal surface strongly (Fig. 10A). In the literature, chemical functionalization of the surfaces is used to promote SERS detection of such nonbinding species [133, 134]. Remarkably, our Ag- HfO_2 -CNT intertwined substrate enabled the detection of Ibu spectra without any chemical functionalization. Compared with the spectra of BPE and BTAH, the concentration-dependent SERS signal does not take a sigmoidal shape or reach saturation (Fig. 10C).

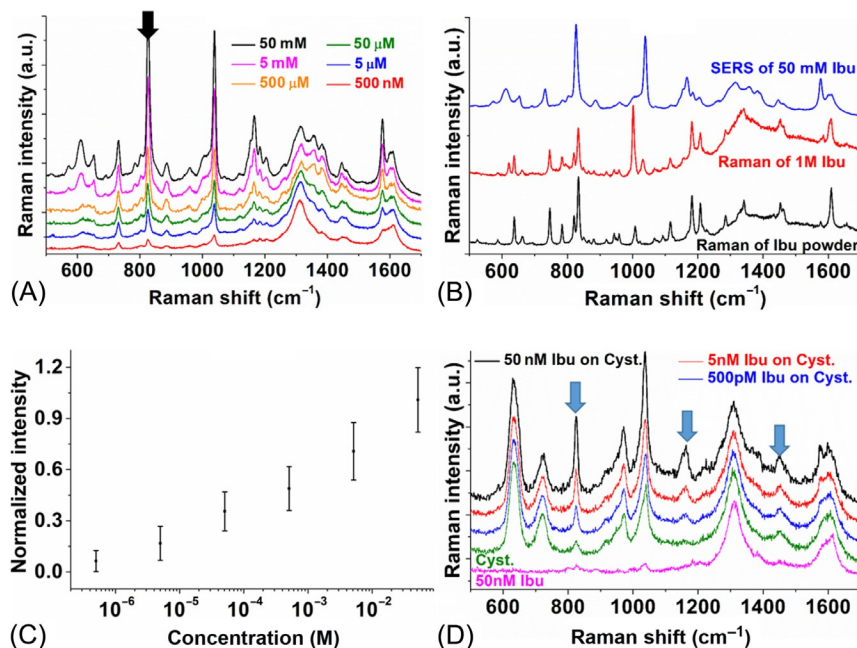


FIG. 10

(A) SERS spectra of Ibu at various concentrations. The detection limit is ~ 500 nM. (B) Comparison between Raman and SERS spectra of Ibu. (C) Concentration-dependent SERS signal of Ibu obtained at 825 cm^{-1} . (D) Improved Ibu detection limit via cysteamine intermediary coating. Grey arrows indicate newly emerging SERS bands inherent to Ibu upon cysteamine coating.

Use of a chemical bridging agent (thiol and amine moieties of cysteamine) greatly enhanced the Ibu detection by three orders of magnitude (>300 pM, Fig. 10D). We attribute the enhanced Ibu detection to two mechanisms: an electrostatic interaction between amine and carboxyl moieties of cysteamine and Ibu, respectively [135], and physical trapping of Ibu onto the steric notch in the cysteamine coating [133, 134]. The cysteamine SERS spectra (Fig. 10D) agrees with the literature, showing representative bands around 636 and 725 cm^{-1} that correspond to *gauche* and *trans* conformers of the S-C-C chain, respectively [135]. Grey arrows indicate bands coming from Ibu. Consequently, the SERS detection of nonbinding species can be enhanced by optimizing the surface functionalization.

In the literature, the sigmoidal trend of the adsorption isotherm has been explained with cooperative adsorption [136, 137] where the adsorbed molecules facilitate an easier adsorption of the others, generally leading to a multilayer coating. However, numerous researches report similar sigmoidal dependencies where the process cannot be explained by the cooperative adsorption alone [110, 115, 116, 138, 139]. As an example, the experimental and computational studies on the adsorption of BPE molecule on the metallic surface do not give any indication of cooperative adsorption [97, 100, 140]. Therefore, the sigmoidal trend calls for another explanation. Here, we propose the

following generalized Langmuir model [141–143] (Eq. 6) to explain the sigmoidal SERS signal with logarithmic concentration:

$$\theta = \frac{\alpha K_{eq} C^n}{1 + K_{eq} C^n} \quad (6)$$

In the formula, C , K_{eq} , and θ are concentration, equilibrium constant of the adsorption, and surface coverage, respectively. When the parameters α and n are equal to unity, Eq. (6) yields to the basic form of the Langmuir model that has the following set of assumptions: (a) The surface is perfectly flat and uniform; (b) all of the adsorption sites are identical; (c) an adsorption site can accommodate only a single molecule; (d) the adsorbed molecule does not diffuse along the surface; and (e) once adsorbed, there is no additional interaction among molecules [144]. Accordingly, this model assumes that all of the adsorption sites will be occupied for the full coverage (Fig. 11).

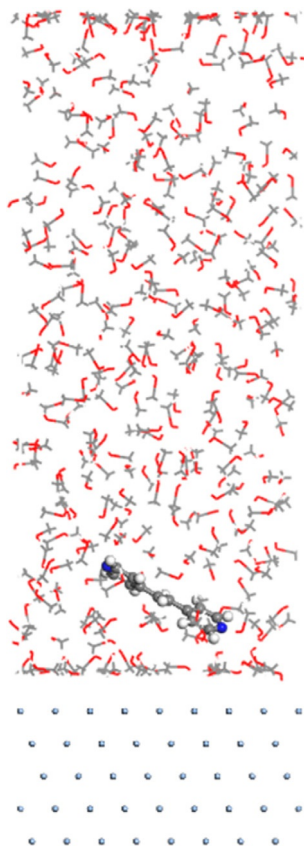


FIG. 11

An example of the simulation cell before running the molecular dynamic simulation. The cell consists of 350 methanol, 1 adsorbent (BPE), and the Ag [111] surface.

We admit that most of the aforementioned assumptions are not valid in the real situation. A rough surface will have narrow notches that restrict covering of all the adsorption sites available on the surface. In other words, such narrow notches, as the potential source of hot spots, may not be directly accessible to the free molecules in the solution. Instead, molecules could still diffuse nearby these sterically hindering hot spots [143, 145]. Such a diffusion-controlled adsorption process imposes the additional parameter, n , in Eq. (6) that can have a value between 0 and 1. For the surfaces imposing significant steric hindrance, n is expected to have a smaller value.

Another important factor to take into account is that diversity of the adsorption configurations of the chemical species cause significant inhomogeneity to the adsorbent–adsorbate interaction. Consequently, there could be unoccupied adsorption sites even at the saturation coverage. This effect can be quantified using a parameter, packing quality: α^{-1} . The parameter α^{-1} should always be smaller than unity. For an ideal case representing the perfect covering, it will be unity. Therefore, the higher the packing quality, the smaller the α is.

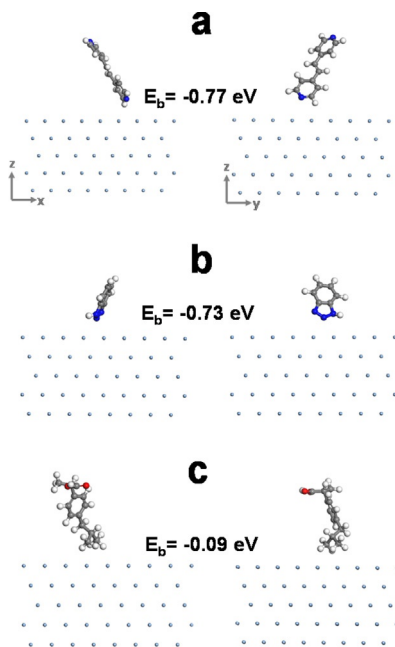
We used the Eq. (6) to fit the concentration-dependent SERS intensities for BPE and BTAH (Fig. 9C and D) successfully. The curve fitting results are summarized in Table 1. Result of the curve fitting for single-compound solutions of BPE and BTAH. The exponent, n , that is related to the adsorption steric hindrance yields a very similar value of 0.38–0.39 for both species. Recollecting the fact that we used similar substrates, fabricated with the identical batch of CNTs, attaining the similar n values is not surprising, for it is a parameter related to the surface morphology of the substrate. It appears that the size difference between BPE and BTAH did not affect the n value considerably. The α^{-1} value of BTAH is slightly larger than that of BPE, indicating that BTAH has a slightly higher packing quality than BPE at their maximum coverage. In fact, as shown later, the minimum-energy configuration of BPE is different from that of BTAH. BPE prefers to stand on the surface with an inclination angle close to 45°. On the other hand, BTAH stands normal to the surface on average to suggest a denser packing.

The K_{eq} values shown in Table 1 imply a stronger binding energy for BPE. To confirm this finding, we carried out molecular dynamic simulations (see Supplementary Materials on <https://doi.org/10.1016/B978-0-12-812667-7.00030-6>). Simulation cells were formed and relaxed before forming a 3D periodic box of 350 methanol atoms with one target molecule (Fig. 12). With the simulation, we determined the binding energy and the minimum-energy configuration of BPE, BTAH, and Ibu on the Ag [111] surface representing our SERS substrate. It should be noted that for face-centered-cubic metals such as Ag [111] planes have the minimum surface energy and the highest surface density, so that the largest surface area is of this crystal orientation [146–148].

Fig. 12(A–C) shows the minimum-energy configurations along with the binding energy values of BPE, BTAH, and Ibu, respectively. BPE adsorbs onto the Ag [111] surface with its nitrogen atom of the

Table 1 Result of the curve fitting for single-compound solutions of BPE and BTAH

Fitting parameters	BPE	BTAH
K_{eq}	1997.1	907.4
n	0.387	0.382
α^{-1}	0.88	0.96
Adjusted R^2	0.992	0.993

**FIG. 12**

Minimum-energy configurations of (A) BPE, (B) BTAH, and (C) Ibu on Ag [111] in the methanol environment. E_b denotes binding energy.

pyridine ring, at an angle of $\sim 45^\circ$. This finding agrees well with the literature reporting on the BPE adsorption on Au via pyridine rings [97]. For BTAH, the nitrogen atoms of the triazole ring play a major role in adsorbing onto Ag, also in good agreement with the literature [131]. The Ibu case is distinct from the other in that oxygen atom of the carboxyl moiety positions closest to the surface to result in the minimum-energy configuration. The calculated binding energy is very small, supporting physisorption as a dominant interaction mechanism between Ibu molecules and SERS substrate.

3.3.2 Competitive adsorption of multiple-compounds

We designed three sets of experiments to carry out a SERS analysis of solution mixtures. Prone to strong binding to Ag, they are likely to compete for the binding sites. The first set of experiment is performed by SERS analyzing solutions of BPE and BTAH (concentration ratio: 125:1, 25:1, 5:1, 1:1, 1:5, 1:25, and 1:125; Fig. 13A and B). The maximum concentration of each compound was 50 nM in this experiment. In order to avoid cross contamination among samples, fresh SERS substrates were prepared at each measurement. The BPE spectrum is invisible when the BTAH concentration is 125-fold higher, while the BTAH spectrum is undetected when the BPE concentration is 25-fold higher. It is obvious that there is an adsorption competition between BPE and BTAH, with BPE slightly dominating the surface occupancy. This result is not surprising, for BPE shows superior detection limit in the single-compound SERS analysis.

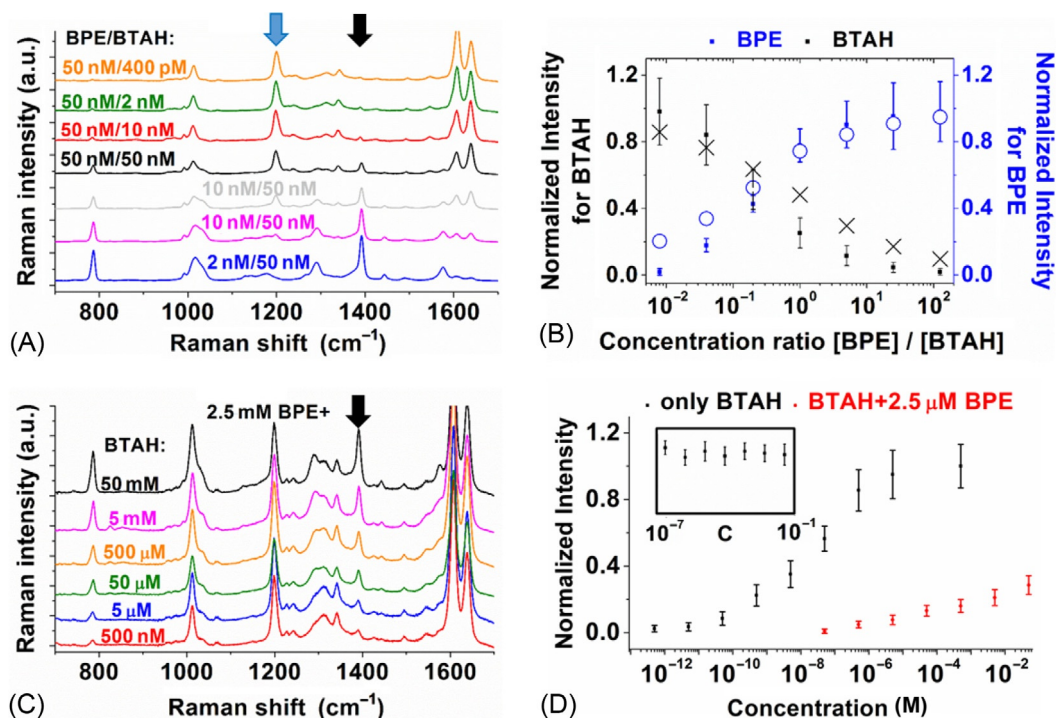


FIG. 13

(A) Multiplexed SERS spectra of a BPE–BTAH mixture of various concentration ratios. Each of the measurement has been made on a fresh SERS substrate. (B) Normalized SERS intensities of BPE and BTAH with respect to the concentration ratio of BPE to BTAH. The cross and round points represent the analytic solution of the multiple-compound competitive adsorption model. The normalization was done with respect to the signal intensities of single-compound solutions of 50 nM concentration. The band intensities at 1200 and 1392 cm^{-1} are selected for BPE and BTAH, respectively. (C) Multiplexed SERS spectra of the BPE–BTAH mixture where BPE concentration is constant (2.5 μM), whereas BTAH concentration varies. One SERS substrate is used for all measurements (in an order from low to high BTAH concentrations). (D) Comparison of the concentration-dependent signal intensity of BTAH in its single species solution and when it is mixed with 2.5 μM BPE. The inset shows the SERS intensity of 2.5 μM BPE at various concentrations of BTAH.

We have modeled the competitive adsorption isotherms again using a generalized Langmuir model. The analytic estimation shows a successful agreement with experimental data except a slight discrepancy for the BTAH-dominant part of the curve. This discrepancy is attributable to the possible effect of the difference of the diffusion constants and the geometry of the molecules that we did not consider in our model.

The second set of experiments is to determine the concentration-dependent SERS response of one species in the abundance of another (Fig. 13C). We ran a SERS analysis by varying the BTAH concentrations over a largely BPE background and vice versa. The measurements began with a mixture of 5-nM BTAH and 2.5- μM BPE and continued by increasing BTAH concentrations every digit up to

50 mM. SERS signal from BTAH is only seen at ≥ 500 nM. It is interesting to observe that the otherwise subpicomolar level detection limit of BTAH becomes degraded almost to the level of a weakly binding species (e.g., Ibu) in the abundance of BPE (Fig. 13D). The signal intensity of BPE did not change with increased BTAH, implying that BPE molecules already adsorbed to Ag are not replaced by BTAHs. We speculate that a BPE coating on the rough Ag surface does not form a perfect packing and BTAH can find certain unoccupied space for adsorption. We performed a similar experiment with varying BPE concentrations at a large BTAH concentration (2.5 μ M, data not shown). Again, the BTAH signal intensity did not change when we soaked the substrate in a solution of various BPE concentrations.

Next, we carried out the final set of experiments on the mixture of weakly and strongly binding species, that is, Ibu and BTAH. As the concentration of BTAH was set at 2.5 μ M, the detection limit of Ibu was not great (25 μ M). Unlike the drastic improvement of the Ibu detection limit by the cysteamine coating, this BTAH intermediary coating actually deteriorates the detection limit by about two orders of magnitude (Fig. 14). Considering the molecular structure, it is unlikely that BTAH offers any physical trapping mechanism to enhance the physisorption of Ibu. In contrast, the existence of BTAH on the surface will primarily consume available sites onto which Ibu to physisorb. This mechanism provides the understanding of the quenching of the Ibu signal.

Giving molecular fingerprints of chemical species and enabling ultrasensitive detection, SERS could serve as a selective and sensitive method suitable for the monitoring of micropollutants. However, this sensitivity depends highly on the chemical environment. If there is a species having high affinity to the SERS substrate, the SERS signal of other species of low affinity will be quenched considerably as a result of competitive adsorption. This effect can hamper the in situ detectability of multiple compounds in food and environmental samples with a single SERS substrate. On the contrary, an ex situ method of detection could be devised. For example, water can be detected commonly from different clean SERS substrates in a sequence, so in the first detection process, the molecule with the strongest binding to metal will be adsorbed leaving the weaker binding molecules to be detected in the next detection step. This sequence can be repeated several times on clean substrates, and hence, stepwise filters out the strongest species adsorbing on the substrate.

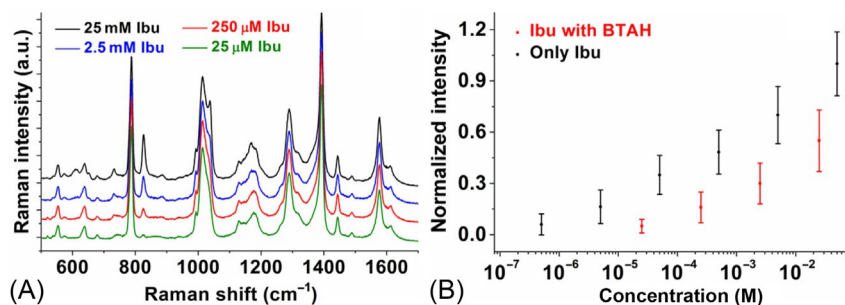


FIG. 14

(A) SERS spectra of Ibu-BTAH mixture. BTAH concentration is set to 2.5 μ M. (B) Comparison of the concentration-dependent signal intensity of Ibu in its single species solution and when it is mixed with 2.5 μ M BTAH.

3.4 SECTION CONCLUSIONS

SERS can lead to femtomolar detection limit for single-compound solutions. This ultrahigh sensitivity implies a potential application of a facile determination of adsorption isotherms for a chemical species having affinity to the SERS substrate over a broad concentration range from femtomolar to micromolar. The concentration-dependent SERS signals for BTAH and BPE describe sigmoidal adsorption isotherms with respect to logarithmic concentration. We employed the generalized Langmuir isotherm model to successfully explain the experimental findings from the mechanistic point of view. The generalized Langmuir isotherm contains three parameters, K_{eq} , α^{-1} , and the exponent n , associated with the binding affinity, packing quality, and the steric hindrance effect, respectively. A molecule with randomly aligned adsorption configuration will result in a lower packing quality (BPE) in comparison with ones having vertical adsorption orientation (BTAH). If the exponent characterizes the steric hindrance effect that renders the adsorption more diffusion-driven, it is likely that a metal surface having tiny notches will result in a small value for n . Similarly, a macromolecule such as DNA or RNA may also lead to a small value of n .

We showed that the generalized Langmuir model can also be used to estimate the competitive adsorption isotherms. Using the values of K_{eq} , α^{-1} , and n extracted from the single-compound isotherms, it is possible to predict and evaluate the competitive adsorption isotherms. This approach can be particularly meaningful because it can save experiments necessary to construct a calibration database for the analysis of multiple-compound mixtures.

The femtomolar detection limit of BPE and BTAH can be partly explained by their strong binding affinities to Ag (a plasmon-active metal in the visible wavelength range), so that even at low concentrations, there can be a sufficient number of molecules adsorbed on the substrate enabling a clear detection. In the case of Ibuprofen of which binding energy is comparable with the thermal energy, the adsorption is much weaker. In such case, very low detection limits cannot be demonstrated due to the small amount of adsorbates. To realize the detection of such weakly binding molecules, proper surface functionalization is necessary. Finally, an important task is to determine SERS-based adsorption isotherms for a target mixture. In this light, the present report places the proof of concept of the SERS-based determination of adsorption isotherms.

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