Electric-Field Enhanced Molecule Detection in Suspension on Assembled Plasmonic Arrays by Raman Spectroscopy

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One of the greatest challenges in surface enhanced Raman scattering (SERS) sensing is to detect biochemicals directly from suspension with ultrasensitivity. In this work, we employed strategically designed longitudinal nanocapsule structures with uniformly surface distributed Ag nanoparticles (Ag NPs) to dually focus and enhance SERS sensitivity of biochemicals in suspension assisted with electric fields. By tuning the reaction conditions, Ag NPs were synthesized and uniformly grown with optimized sizes and junctions on the surface of nanocapsules for well reproducible detection. The Ag NPs can further concentrate molecules from suspension due to induced electrokinetic effects in electric fields. As a result, the signals of Nile blue molecules can be enhanced by $34.4 \pm 3.1\%$ at optimal alternating current (AC) frequencies and voltages compared to that without electric fields. This work demonstrates the dual roles of a new type of plasmonic NPs for molecule concentration and detection, which could inspire new Raman sensing devices for applications in microfluidics. [DOI: 10.1115/1.4030769]

1 Introduction

In the last decade, the technique of SERS has been intensively studied due to its great potentials for label-free and multiplex detection of biomolecules [1–3], pollutants [4,5], and chemical warfare agents [6–8]. When light interacts with noble metal NPs with very narrow junctions, the conduction-band electrons in the NP can collectively oscillate and generate localized surface plasmon. As a result, substantially enhanced electric fields are created in the vicinity or junctions of the NPs, which are also called hot spots. If the analyte molecules are in the hot spots, their Raman signals can be dramatically increased by 10^8 – 10^{12} times [9], which is sufficient for detecting single molecules of various species [10,11]. Previously, different types of SERS substrates were fabricated including metals with roughened surfaces [12,13], nanowires [14,15], metal NPs [16,17], sharp tips [18,19], and core/shell nanospheres [20,21]. However, most SERS detections were carried out by drying analyte solutions on the SERS substrates to force molecules to get into hotspots before the detection. The employed drying methods can be different among individual research groups. Quantitative comparison of these results should be conducted carefully. Given the same employed equipmental conditions, it is highly desirable to directly detect molecules in suspension to accurately evaluate the performances of different SERS substrates, which will also have pivotal implications for SERS biosensing in microfluidics. However, when directly detecting from solutions, we found that with the same SERS substrate, the lowest detection limit of molecules at the same experimental and equipmental conditions, such as Rhodamine 6G (R-6G) and Nile blue, commonly used SERS probes, can be higher by a few orders of magnitudes compared to that from samples with dried molecule probes [11,22]. Therefore, it is of great interest to investigate new mechanisms to detect biochemicals directly from solutions with high sensitivity.

Electrokinetic phenomena due to AC and direct current electric fields applied on designed microelectrodes have generated

immense interest in manipulation of NPs, live cells, and even biomolecules [23]. Recently, it was applied on prepatterned plasmonic substrates, such as Au nanoholes [24], microneedles [25], nanopillars [26], and nanospheres [27,28] to focus analyte molecules to the hotspots before optical detection. Nevertheless, most previous efforts either require complex lithography for fabricating SERS-active entities [25–27] or could not precisely control the sizes/junctions of plasmonic particles for high reproducible detection when electric fields are applied [27].

In this work, we report electric-field enhanced molecule detection from an innovative type of SERS-active nanocapsule structures. The nanocapsules can be bottom-up synthesized in a large scale, dynamically assembled into ordered arrays, and offer a large number of hotspots with controlled sizes owing to the unique design of the structures. With optimized AC frequencies, voltages, and structure of the microelectrodes, biomolecules, including those having low molecular weights such as Nile blue, can be effectively concentrated on the surface of the nanocapsules. The Raman signal of Nile blue can be improved by $34.4 \pm 3.1\%$ after applying the electric field for a few minutes. This work could inspire the next generation microfluidic based Raman sensing devices.

2 Results and Discussion

The nanocapsules consist of a trilayer structure with a gold nanowire in the core, a thin silica layer on the surface of the nanowire core, and high-density Ag NPs grown on the silica layer providing Raman-sensitive hot spots (Scheme 1). Each layer in the nanocapsule serves for a specific purpose: the inner metallic nanowire core can be readily polarized in electric fields and manipulated by dielectrophoretic (DEP) forces [11,29]; the silica layer supports the synthesis of the Ag NP arrays, which also effectively eliminate possible plasmonic quenching between the Ag NPs and the metallic nanowire. The Ag NPs in the outmost surface have optimized sizes, density, and uniformity and can effectively detect R-6G molecules dried on the surface with single molecule sensitivity [11,22].

The fabrication of nanocapsules starts with the electrodeposition of Au nanowires in nanoporous membranes. In brief, Au

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Scheme 1 (a) The cross section schematic diagram of a nanocapsule where a metallic Au nanowire serves as the core, a silica layer grown on the surface of the metal core support the Ag NPs growth and Ag NPs uniformly grow on the silica layer. (b) Side view scheme of a nanocapsule.

Fig. 1 Scanning electron microscopy (SEM) images of (a) arrays of Au nanowires with an average length of $8.5\ \mu\text{m}$ and diameter of $300\ \text{nm}$, (b) Au nanowire encapsulated by a $180\ \text{nm}$ thick silica layer, and (c) SEM images of Au/silica nanocapsules coated with Ag NPs (the zoom-in images of Ag NPs are shown in Fig. 2.)

Fig. 2 SEM images of nanocapsules fabricated at different conditions with reactant concentrations and volumes as: (a) AgNO_3 ($0.06\ \text{M}$, $350\ \mu\text{l}$): $\text{NH}_3\cdot\text{H}_2\text{O}$ ($0.12\ \text{M}$, $175\ \mu\text{l}$), (b) AgNO_3 ($0.06\ \text{M}$, $400\ \mu\text{l}$): $\text{NH}_3\cdot\text{H}_2\text{O}$ ($0.12\ \text{M}$, $200\ \mu\text{l}$), (c) AgNO_3 ($0.06\ \text{M}$, $500\ \mu\text{l}$): $\text{NH}_3\cdot\text{H}_2\text{O}$ ($0.12\ \text{M}$, $250\ \mu\text{l}$), and (d) AgNO_3 ($0.06\ \text{M}$, $600\ \mu\text{l}$): $\text{NH}_3\cdot\text{H}_2\text{O}$ ($0.12\ \text{M}$, $300\ \mu\text{l}$)

nanowires were electrodeposited from commercially available cyanide based electrolyte (434 HS RTU; Technic, Inc., Cranston, RI). The diameter of the nanowires can be controlled by the size of the nanopores from tens of nanometers to $400\ \text{nm}$, and the

length of the Au nanowires is determined by the amount of electric charge passing through the circuit. After dissolving the membrane, the nanowires were resuspended and sonicated in ethanol and deionized (D.I.) water alternatively twice before redispersed

Fig. 3 Raman detection from nanocapsules in 100 μM R-6 G suspension. (a) Well repeatable Raman signals from nanocapsules synthesized in the same batch with volumes of AgNO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$ as 500 μl : 250 μl . (b) Comparison of Raman signals from samples fabricated at different conditions with volumes of AgNO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$ as 400 μl : 200 μl (black) 500 μl : 250 μl (red), and 600 μl : 300 μl (blue).

in D.I. water. Billions of nanowires can be fabricated at a time with length of 8.5 μm and diameter of 300 nm as shown in Fig. 1(a). Next, a 180 nm thick SiO_2 layer was coated on the surface of the Au nanowires via hydrolysis of tetraethyl orthosilicate (TEOS, 0.8 ml; Alfa Aesar, Ward Hill, MA, 99.999+%) in ammonia (0.2 ml; Fisher Scientific, Certified A.C.S. Plus, Pittsburgh, PA), ethanol (6 ml; Pharmco-aaper, ACS/USP grade, Brookfield, CT), and deionized water (3.6 ml) for 1 hr (Fig. 1(b)). Finally, Ag NPs were synthesized on the surface of silica by mixing Au/ SiO_2 nanowires with freshly prepared silver nitrate (AgNO_3 ; Acros Organics, Belgium, 99.85%), and ammonia, stirring for 1 hr before adding polyvinylpyrrolidone (PVP, 10 ml of 2.5×10^{-5} M in ethanol; Sigma-Aldrich, St. Louis, MO, $M_w = 40,000$) to catalyze the growth of Ag NPs at 70 $^\circ\text{C}$. After 7 hrs reaction, dense Ag NPs were obtained on the entire surface of the nanocapsules as shown in Figs. 1(c) and 2.

Since SERS enhancement highly depends on the sizes of Ag NPs, their junctions, and NP distribution [30], we systematically varied the reaction conditions to tune the morphology and dispersion of Ag NPs and measured the corresponding SERS performance. As shown in Figs. 2(a) and 2(b), if the volumes of AgNO_3 (0.06 M) and $\text{NH}_3\cdot\text{H}_2\text{O}$ (0.12 M) are relatively low (350 μl : 175 μl or 400 μl : 200 μl) when mixed with 400 μl Au/ SiO_2 nanowire suspension in D.I. water, the Ag NPs grow sparsely on the surface of the nanocapsules. If the volumes of AgNO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$ are increased to 500 μl : 250 μl or 600 μl : 300 μl , dense arrays of Ag NPs can be fabricated uniformly along the length of the nanocapsules as shown in Figs. 2(c) and 2(d). The sizes of Ag NP and junctions are 30.1 ± 12.8 nm and 2.00 ± 0.45 nm, respectively, for reactants of AgNO_3 (500 μl) and $\text{NH}_3\cdot\text{H}_2\text{O}$ (250 μl). When the volumes of AgNO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$ are changed to 600 μl : 300 μl , the sizes of Ag NPs and junctions increased to 39.4 ± 13.1 nm and 2.57 ± 0.70 nm, respectively.

With Ag NPs coated on the surface of nanocapsules, we characterized their SERS performances. As aforesaid, previously SERS characterizations were often conducted by using SERS probes naturally dried on the NPs surfaces. There are many uncontrollable factors during the drying process, which could make it difficult to compare the characterizations obtained by different groups or individuals. In this work, we evaluated the SERS performances by directly immersing the as-prepared nanocapsules in a suspension of a commonly used SERS probes, R-6 G, with known concentrations (Acros Organics, 99%, 100 μM). A customized Raman microscope equipped with a 633 nm laser was used for Raman characterization. Well reproducible SERS signals were obtained from different nanocapsules synthesized in the same

batch of AgNO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$ solution with volumes of 500 μl and 250 μl , respectively (Fig. 3(a)). Such SERS intensity is the highest among all the samples with different volumes of reactants (Fig. 3(b)). It indicates that nanocapsules with an average particle and gap sizes of 30.1 ± 12.8 and 2.00 ± 0.45 nm, respectively, offer the best SERS performance (Fig. 2(c)), which agrees with the simulation results reported in our previous work where the highest electric field in the hotspots is generated from Ag NPs with the narrowest junctions and diameters of 30–50 nm [22].

Not only providing well reproducible SERS enhancement, the nanocapsules can be efficiently assembled into ordered arrays by electric fields owing to the strategically embedded metallic cores that can be strongly polarized in AC electric fields. Different from previous work, the feature sizes and distribution of the SERS-active components, Ag NPs, remain intact during the manipulation and assembling process [27]. Specifically, before the assembling of nanocapsules, a layer of polymethyl methacrylate (PMMA; MicroChem, Westborough, MA, 950 k C2) was spin-coated on the microelectrodes to maintain the mobility of the nanocapsules. Then the nanocapsules were suspended randomly in a polydimethylsiloxane (PDMS) well. Upon the application of

Fig. 4 (a) Schematic diagram of nanocapsules assembled on interdigital microelectrodes, (b) the attraction of molecule to the nanocapsules with the electric fields, (c) Raman image of Nile blue molecules (with background fluorescence of Nile blue molecules and Ag NPs) on arrays of assembled nanocapsules on microelectrodes (enhanced image), and (d) the corresponding optical microscopy image

Fig. 5 (a) Raman spectrum of Nile blue (250 nM) detected from a nanocapsule in solution, which demonstrated that 595 cm^{-1} was the most prominent Raman peak and well separated from others. (b) Frequency dependent Raman intensity enhancement at 595 cm^{-1} of Nile blue molecules (100 nM) recorded after applying an electric field at 20 V and 200 kHz to 1 MHz (the curve in orange is an eye guide.)

the electric field at 700 kHz and 20 V on the interdigital indium tin oxide (ITO) microelectrodes (gap size: $20\text{ }\mu\text{m}$), the nanocapsules were swiftly attracted to the edges of the microelectrodes and aligned in the direction of the electric fields as shown in Figs. 4(a) and 4(b). Essentially, they spaced evenly with approximately $6.6\text{ }\mu\text{m}$ due to the electrostatic repulsion in neighboring nanocapsules [31,32].

The transportation and assembling of nanocapsules can be attributed to DEP forces resulted from the interaction between the electric field and polarized nanocapsules, given by [33]

$$F = p \cdot \nabla E, \quad (1)$$

where the polarization of the nanocapsules (p) is proportional to the applied electric fields and depends on the chemistry and geometry of the nanocapsules. The transport and orientation of the nanocapsules are in the directions of the electric-field gradient and electric field, respectively [34].

After assembling arrays of nanocapsules, we turned off the AC voltages and carefully dispersed $10\text{ }\mu\text{l}$ Nile blue (Alfa Aesar, Inc.) solution with a concentration as low as 100 nM into the PDMS

Fig. 6 Time dependent Raman intensity at 595 cm^{-1} of Nile blue molecules (100 nM) recorded before and after applying an electric field at 200 kHz (a) 5 V, (b) 10 V, (c) 15 V, and (d) 20 V

Fig. 7 Time dependent Raman intensity of Nile blue molecules (100 nM) at 595 cm^{-1} recorded when the E -field is turned on and off alternatively at 20 V, 200 kHz

well. The Raman images of Nile blue on nanocapsule arrays with fluorescent background of Nile blue and Ag NPs were collected after a 633 nm edge filter as shown in Fig. 4(c). The corresponding optical image is shown in Fig. 4(d). Then, the Raman spectra of Nile blue were recorded from the nanocapsules for 300 s with an integration time of 1 or 2 s from a $50\times$ objective lens before an AC electric field was applied. The peak height at 595 cm^{-1} was used for analysis since it was the most prominent peak and well separated from others (Fig. 5(a)). AC electric fields with frequencies ranging from 200 kHz to 1 MHz were studied as shown in Fig. 5(b). The strongest attraction was achieved at 200 kHz (Fig. 5(b)). As soon as the electric field was applied, the intensity of Raman signal rapidly increased and reached the saturation in ~ 100 s at 20 V (Fig. 6(d)). Compared with the peak intensity without the electric field in the first 300 s, the Raman peak intensity increased by $\sim 35\%$ in total due to the electric field. The result is well repeatable. Within different trials, the average increment of Raman intensity is $34.4 \pm 3.1\%$. Moreover, we also systematically tuned the amplitude of the applied E -field at 200 kHz from 5 V to 20 V (Fig. 6). When we applied 5 V, the Raman signal did not change obviously; when we increased the applied voltage from 5 V to 10 V and 15 V, the Raman signal increased to 10.9% and 24.4%, respectively. Note that for the comparison purpose, we normalized the Raman intensity before the E -field was applied. To further confirm the effect of the electric field, we cycled the application of the AC E -field at 20 V, 200 kHz. It shows that the enhancement of Raman detection can be essentially restored when the electric field is turned on again. The enhancement values are 31.5% and 31.6% for the first and second cycle, respectively (Fig. 7). The enhancement is attributed to the attraction of the Nile blue molecules to the hot spots on the nanocapsules due to the induced electric fields in the narrow junctions of Ag NPs. Different electrokinetic mechanisms can play roles. First, we notice that AC electroosmosis (ACEO) flows could be induced by the electric field, where liquid flows circulate around the metallic NPs due to the interactions of the electric field and the electrical double layers next to the surface of the NPs [35]. Such flow can bring analyte molecules to the vicinity of the nanocapsules. When the molecules are close to the nanocapsules, the high intensity of the induced electric field at the junctions of Ag NPs can further attract them to the hotspots due to the DEP effect given by Eq. (1) and increase the SERS detection sensitivity. This understanding is supported by previous work [36] and quantitatively studied in the manipulation of solid-state molecules [37]. We noticed that the average Raman intensity before the E -field was applied in the second cycle decreased by $\sim 5\%$ compared to that in the first cycle, which could be attributed to the possible photo bleaching of the dye molecules or unknown factors that need further investigation.

3 Conclusions

In summary, we synthesized an innovative type of nanocapsule structures with large number of hotspots. By tuning the reaction conditions, we achieved optimized sizes of Ag NPs and junctions between the Ag NPs, which can detect biochemicals directly from suspensions with high reproducibility. After strategically assembling the as-grown SERS nanocapsules into ordered arrays on microelectrodes, we detected biochemicals such as Nile blue in a location deterministic manner. Moreover, assisted with electric field, we further enhanced the intensity of Raman signals by $34.4 \pm 3.1\%$ at optimal frequencies and voltages compared to those without electric fields. The enhancement mechanisms are discussed. Therefore, we demonstrated a new type of plasmonic nanosensors with dual functions for attracting molecular analytes and enhancing their Raman signals owing to the uniquely designed nanostructures. This work could be inspiring for new types of microfluidic integrated SERS nanosensors.

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