Superhydrophobic needles tipped with 2-dimensional arrays of plasmonic colloidal nanoparticles for microdroplet SERS analysis


Published in:
Journal of Raman Spectroscopy

Document Version:
Publisher's PDF, also known as Version of record

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Publisher rights
© 2020 The Authors.
This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Open Access
This research has been made openly available by Queen's academics and its Open Research team. We would love to hear how access to this research benefits you. – Share your feedback with us: http://go.qub.ac.uk/oa-feedback
Superhydrophobic needles tipped with 2-dimensional arrays of plasmonic colloidal nanoparticles for microdroplet SERS analysis

Chunchun Li | Lin Chai | Qinglu Chen | Ziwei Ye | Yikai Xu
Steven E.J. Bell

School of Chemistry and Chemical Engineering, Queen’s University Belfast, Belfast, UK

Correspondence
Yikai Xu, School of Chemistry and Chemical Engineering, Queen’s University Belfast, Belfast BT9 5AG, UK.
Email: yxu18@qub.ac.uk

Steven Bell, School of Chemistry and Chemical Engineering, Queen’s University Belfast, Belfast BT9 5AG, UK.
Email: s.bell@qub.ac.uk

Abstract
Aqueous microdroplets strongly attach to metallic needles with superhydrophobic sides and flat hydrophilic tips. Such needles can be made surface-enhanced Raman spectroscopy (SERS)-active by adsorbing a layer of densely packed and uniform plasmonic nanoparticles onto the hydrophilic tip. The resulting particle-tipped needles allow dual enhancement of the Raman signals from microdroplets of low concentration analytes by combining analyte enrichment through solvent evaporation and plasmonic SERS enhancement. The combination of small sample volume, preconcentration, and SERS allows extremely low total amounts of analytes to be detected. Here, we show that with crystal violet as the model analyte, the limit of detection can reach 2 pg. The method can be readily used to fabricate superhydrophobic needles tipped with different types of plasmonic colloidal nanoparticles for enhanced Raman analysis, for example, silver cube tipped needles could be used to detect as little as 2.5 ng of trinitrotoluene.

KEYWORDS
plasmonics, self-assembly, SERS, superhydrophobic, TNT

1 | INTRODUCTION

Due to its ability to carry out rapid, nondestructive, molecularly specific measurements, Raman spectroscopy is widely used for chemical analysis in fields that range from biomolecular imaging to forensic analysis [1–4]. These advantages are most obvious with portable handheld Raman spectrometers, where spectra may be conveniently obtained outside conventional laboratory settings [5, 6]. However, a crucial disadvantage of Raman spectroscopy is its poor sensitivity compared with most competing analytical techniques due to the inherently low Raman scattering cross-sections of most materials and compounds [7]. With small absolute amounts of solid samples, this problem can be largely overcome by using state-of-the-art Raman microscopes which focus the probe laser to a sub-micrometer dimension spot and allows micrometer dimension sample particles to be studied with ease [8, 9]. However, even high-power Raman microscopes become powerless when the analyte is both present in small quantities and homogeneously dispersed in an aqueous solution, which is often the case.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2020 The Authors. Journal of Raman Spectroscopy published by John Wiley & Sons Ltd

J Raman Spectrosc. 2020;1–8.
The most straightforward method to increase the signal of analytes in solution is to evaporate some, or all, of the solvent. However, this approach does have problems, most notably the formation of “coffee-rings” which make absolute quantification difficult due to the large variations in sample distribution at different points of the dried deposit [10]. This issue can be addressed by using substrates which minimize pinning of the drying droplet so that the droplet shrinks radially during drying, ideally leaving a very small concentrated deposit at a single point on the surface. Typical examples of this approach include the use of superhydrophobic (SHP) substrates and, more recently, materials with “slippery” surfaces in which the aqueous analyte droplet is dried down on a thin layer of immiscible liquid constrained within the textured surface of a supporting substrate [11–13]. However, one problem with nonpinning surfaces is that the location of the final deposit is poorly controlled unless some mechanism is used to direct the droplet to a specific location. This can be achieved by using lithographically etched patterns on substrates but is complex and expensive [14]. To combat this, we have previously developed substrates for droplet drying which use a SHP needle with a hydrophilic tip [15]. In use, the analyte droplet can be simply applied onto the tip of the needle and, due to the hydrophobic walls of the needle, will remain in place during evaporation, ultimately leaving the solid deposit in a very well defined region, that is, the tip of the needle. This approach allowed Raman detection of challenging analytes such as sucrose and glucose dried from solutions at ca. mM concentrations without any other form of enhancement.

Another popular approach for Raman analysis of low concentration analyte solutions is to use surface-enhanced Raman spectroscopy (SERS), which utilizes the surface-plasmon of Ag and Au nanoparticles to increase the scattering signal of the analyte molecules adsorbed on the plasmonic particle surfaces [16–18]. In this context, we have shown that the SHP needles can be used as convenient supports to host small droplets (less than 1 μL) of solution which contain both the analyte of interest and colloidal Ag nanoparticles for SERS detection of dipicolinic acid (a proxy for Bacillus anthracis [anthrax] spores) down to 10^{-6} M [19]. Although successful, this approach requires delicate sample handling steps and does not take full advantage of the SHP needles’ ability to concentrate analytes in solution. Here, we report the next step in the development of SHP needles where a densely packed and uniform layer of nanoparticles are dip-coated onto the hydrophilic tip of the SHP needles. In this case, the analyte solution can simply be applied as a drop onto the plasmonically active tip and allowed to dry onto the enhancing surface to generate strongly enhanced Raman signals, which combines the advantages of sample preconcentration and surface enhancement in a single substrate. Using crystal violet (CV) as the probe analyte and conventional hydroxylamine-reduced Ag nanoparticles, we found that the limit of detection (LOD) could reach 2 pg. Moreover, we have also shown that the method can be readily applied to produce plasmonic SHP needles carrying other types of plasmonic colloidal nanoparticle layers, which can lead to further improved SERS performance for the detection of important analytes, such as trinitrotoluene (TNT).

2 | METHODS

2.1 | Materials

All chemicals used were purchased from Aldrich Ltd. and used without further purification unless otherwise stated. Copper wires 220 μm in diameter were purchased from wires.co.uk Ltd and used as received. All solutions were prepared from distilled, deionized (DDI) water (resistivity = 18.2 MΩ), obtained from a Branstead Nanopure system.

2.2 | Colloid preparation

Citrate-reduced Ag colloid, hydroxylamine-reduced Ag colloid, mono-disperse citrate-reduced Au nanospheres, mono-disperse Ag nanospheres, Ag nanocubes were prepared following literature protocols [20–24].

2.3 | Preparation of 2-D nanoparticle arrays

Two-dimensional (2-D) interfacial nanoparticle arrays were prepared following our previously reported method [25]. In brief, 5 ml of aqueous colloid was vigorously shaken with 3 mL of dichloromethane (DCM) in the presence of 0.13 mL of 10^{-3} M of tetrabutylammonium nitrate “promoter” for ca. 1 min, which led to the formation of a 2-D film at the liquid–liquid interface. Polyvinylpyrrolidone (PVP, 25000 M.W.) capped nanoparticle arrays were prepared by shaking the 5 mL of colloid with 0.5 mL of 10^{-3} M of PVP solution for 1 min followed by shaking the colloid with DCM and promoter via the same procedure described above.
2.4 | Preparation of SHP needles

SHP needles were prepared using electroless galvanic deposition [15, 26]. This involved coating Cu wires of different diameters with a textured Ag layer by immersing in aqueous solution of silver nitrate (0.01 M) for ca. 1 min. After this, the wires were allowed to dry naturally in air. Then, they were immersed into a solution of 1H,1H,2H,2H-perfluorodecanethiol (HDFT) in DCM (0.001 M) for ca. 5 min and allowed to dry in air. Finally, the SHP copper wires were cut by a sharp scalpel to create a hydrophilic tip.

2.5 | Preparation of plasmonic SHP needles

Plasmonic SHP needles were prepared by dipping the hydrophilic tip of the as-prepared SHP needles vertically into 2-D nanoparticle arrays twice and then allowing them to dry naturally in air.

2.6 | SERS analysis

Samples for SERS analysis were made by applying 1 μL of different concentrations of aqueous analyte solution onto the particle-coated tip of the plasmonic SHP needles (220 μm in diameter) using a glass gas chromatography (GC) sample injection syringe and allowing them to dry. The metal needle of the GC injector was made SHP to allow transfer of the sample droplet onto the plasmonic SHP needle. Briefly, this was achieved by electroplating a layer of copper onto the surface of the needle. After this, the copper-coated injector needle was rendered SHP using the same protocol as that used for fabricating SHP needles as described above. SERS spectra were collected using a PerkinElmer RamanMicro200 Raman microscope equipped with a 10× objective and 785 nm laser (10 mW laser power and 60 μm spot diameter). All spectra were collected at a random point of the enhancing surface with 50 s accumulation time. All spectra were processed using Grams AI software.

2.7 | SEM analysis

Scanning electron microscopy (SEM) was performed with a Quanta FEG 250 at an acceleration voltage of 20 kV under high chamber vacuum (<8 × 10⁻⁵ mbar) with standard SEM copper tape as background.

3 | RESULT AND DISCUSSION

The first step in preparation of the plasmonic SHP needles is to create a SHP needle with a hydrophilic tip. As we have previously reported, this is surprisingly straightforward, a Cu wire is first given a SHP coating by immersing it in a AgNO₃ solution, which causes electroless deposition of a rough fractal layer of metallic Ag. A low surface energy self-assembled monolayer is then created on the surface of the Ag nanostructures by immersing the wire in a polyfluorothiol solution, the combination of high roughness and low surface energy means the coating has an extremely high contact angle (greater than 170°) [26]. The hydrophilic tip is then created by cutting the wire to leave a bare Cu metal face (Figure S1). With these needles, microliter water droplets will sit on the tip as millimeter diameter spheres which are fixed firmly in place because they are pinned to the bare needle tip and are prevented from running down the sides of the support by the SHP coating [15].

To introduce a densely packed layer of plasmonic nanoparticles onto the hydrophilic tip of the SHP needles, colloidal plasmonic nanoparticles were assembled at the water-DCM interface by shaking a mixture of negatively charged aqueous colloid, DCM and positively charged “promoter” ions (see Section 2 for details), as illustrated in Figure 1a,b [25]. When the preparation is carried out in a hydrophobic polymer container, the DCM phase preferentially wets the container surface to form an encapsulating layer around the aqueous phase [27, 28], as shown in Figure 1b, so the interfacial nanoparticles also wrap as a sheet around the upper aqueous layer. To coat the SHP needles with particles, they were pushed directly through this interfacial nanoparticle film from above. As shown in Figure 1c, when the tip reaches the aqueous layer a small quantity of water adheres to it and, importantly, remains attached to the hydrophilic surface when the needle is pulled back through the interface and into the upper DCM layer, as shown in Figure 1d,e. This creates a new water-DCM interface on the tip of the needle which is coated with a layer of nanoparticles that stays on the needle tip even as it is withdrawn through the oil layer and out into the air, at which point it can be clearly observed by the naked eye as a reflective metallic liquid dome. This submicroliter volume droplet dries within minutes in air, which brings the interfacial nanoparticles layer down as a uniform and densely packed plasmonic coating onto the hydrophilic tip of the SHP needles, as shown in Figure 1f,g. Figure 2 shows SEM images of the SHP side wall of the needle with its fractal Ag layer and the layer of deposited Ag nanoparticles on the tip after drying. The figure also includes an optical image showing a sample
droplet pinned to the tip of a vertical needle which is initially spherical and ca. 4 × the diameter of the tip before evaporation. The uniformity of the SERS signal of the dry Ag nanoparticle layer was measured using the 948 cm⁻¹ band of the citrate capping layer which the particles carry, recording data at 20 points on the surface gave a relative standard deviation of ca. 24% whereas the difference in the average value between two different plasmonic SHP needles was less than 5%, which showed that the dip-coating approach generated uniform enhancing layers with extremely high reproducibility. The enhancing particle layer was also found to be well attached to the surface of the SHP needle because there was no detectable difference between the SEM images of tips before and after immersion in stirred water for 30 min followed by drying (Figure S2). This is important because it means that the particles do not detach under the conditions which they would be expected to encounter in common sensing applications, where the plasmonic SHP needle is either dipped into a sample solution or when a droplet of sample solution is dried onto the tip.

Surprisingly, when a 0.6 μL droplet of 10⁻⁷ M CV solution was placed onto a nanoparticle coated tip and allowed to dry, the resulting deposit did not give a detectable SERS signal, despite the fact that this process produced a deposited layer of dye on the surface which could be observed by SEM and gave a noticeable purple tint to the nanoparticle coated tip (Figures S3 and S4). The origin of this lack of signal was not simply that CV gives low signals with these nanoparticles because we and other research groups have shown that the parent interfacial metal films give very strong SERS enhancement both in situ and as films deposited onto planar substrates, such as a quartz slide [27–34].

One possible explanation for this low enhancement is that during the drying process, the particles become jammed together to such an extent that the analyte molecules are not able to access the active hot spots at the junction between them. More specifically, within the interfacial layer, the balance of attractive and repulsive forces between the particles allows them to sit at a distance which is sufficiently close to allow the plasmonic coupling necessary for enhancement while still allowing the analyte free access to the “hot spots” which this creates. However, in the preparation method used here, simple geometry requires that the surface area of the domed droplet which is initially attached to the tip will be larger than that of the flat substrate it dries down onto. Therefore, in the evaporation step the particles will be forced to be closer together than they were at the liquid–liquid interface [35]. Jamming the particles together in this way may reduce the access to the plasmonically active regions between the particles to such an extent that the analyte is prevented from entering them. Consistent with this
explanation, we note that strong SERS signals of CV were obtained from the dried deposit if the CV analyte was added to the particle-covered droplet before it was dried down onto the SHP needle tip (Figure S5). Presumably because adding the CV molecules at this point allowed them to adsorb onto the particles and therefore be located at the hot spots before the nanoparticles were completely jammed together.

It was found that this problem could be solved by preparing the parent interfacial nanoparticle array in the presence of PVP, which is known to act as a spacer between nanoparticles [36]. This is not important when the films are used at the interface but has a very significant effect on the performance of the system when the particle films are dried out on the surface of the SHP needles. As illustrated schematically in Figure 3, addition of PVP can maintain the separation of the 2-D nanoparticles in the array even after they are dried down on the surface of the needle at the value which is close enough to generate intense plasmonic coupling but also large enough so that the plasmonic hot spots are easily accessible to analytes. The additional spacing is too small to be resolved by SEM, so images of films prepared with and without PVP are indistinguishable (Figure S6) but the effect on the SERS response is dramatic. As shown in Figure 3 (spectrum i), strong CV signals can be observed when 1 μl of 10^{-6} M CV is dried onto a plasmonic SHP needle made with PVP-capped citrate-reduced Ag nanoparticles, whereas no CV signals were observed when untreated citrate-reduced Ag nanoparticles were used (spectrum ii).

Importantly, this method of using PVP as a steric spacer can be generally applied for different types of plasmonic nanoparticles because PVP has a strong affinity to Ag and Au colloids, which allows a very broad range of plasmonic nanoparticles to be used for the preparation of plasmonic SHP needles. In the current study, we have prepared SHP needles tipped with PVP-capped nanoparticles using hydroxylamine reduced Ag colloids, mono-disperse Ag and Au colloids prepared by seeded growth and Ag nanocubes, as shown in Figure 4.

To further test the enhancement provided by the plasmonic SHP needles, concentration dependent detection of CV was carried out. In these experiments, hydroxylamine-reduced Ag nanoparticles were used because their blank background spectrum has fewer features than citrate-reduced Ag nanoparticles. A plot of the
SERS intensity of the characteristic CV vibration band at 1,178 cm$^{-1}$ versus the concentration of the sample droplet solution (Figure 5) shows that the signal for a $5 \times 10^{-8}$ M solution could be detected and that the system saturated at a concentration of $5 \times 10^{-7}$ M before falling in intensity at higher concentration, possibly due to interference from excess CV crystals. The dual enhancement provided by combining physical preconcentration and plasmonic-enhancement allowed signals of CV dried from 1 μL droplets of solution to be detected down to $5 \times 10^{-8}$ M, which corresponded to just 20 pg of CV. The stability of the plasmonic SHP needles was also studied using CV as the model analyte. As shown in Figure S7, ca. 50% of the SERS activity of the SHP needles were retained when left exposed in air for 1 week.

Another practical advantage that comes with using plasmonic SHP needles for enhanced Raman detection is that the Cu support which is important for providing the base for the SHP coating also acts as a heat sink, which allows relatively high laser power to be used to record spectra without burning the sample or substrate. The associated increase in intensity corresponds to a lower detection limit. For example, when the laser power was increased to 18 mW, the detection limit of CV was improved by an order of magnitude to $5 \times 10^{-9}$ M, which corresponded to just 2 pg of CV (Figure S8).

The plasmonic SHP needles have also been tested with a more challenging target, TNT, which is often used as a model for explosive detection [37–40]. Here, 2-D arrays of PVP-capped Ag nanocubes were used as the
enhancing layer for stronger plasmonic enhancement. Figure 6 shows data obtained from small (1 μL) volumes of dilute aqueous TNT solutions. The samples show the characteristic broad nitrate scattering peak at ca. 1,350 cm$^{-1}$ superimposed on the broad background features which are associated with these enhancing nanoparticles. Despite the interference from this background, the nitrate peak is clearly detectable in unmanipulated data for 1.1 × 10$^{-5}$ M TNT. This corresponded to just 2.5 ng of explosive, which is three orders of magnitude lower than the established risk-based screening level of TNT in tap-water in the United States [41]. Similarly, biomolecules of interest, such as adenine can also be detected using plasmonic SHP needles as shown in Figure S9.

**FIGURE 5** (a) Surface-enhanced Raman spectroscopy (SERS) signals of crystal violet (CV) obtained by drying 1 μL of different concentrations of CV solution onto plasmonic superhydrophobic (SHP) needles coated with two-dimensional (2-D) arrays of polyvinylpyrrolidone (PVP)-capped hydroxylamine-reduced Ag nanoparticles. (b) Plot showing the intensity of the CV peak at 1,178 cm$^{-1}$ against the concentration of CV solution. The intensity for each data point were averaged from five independent measurements.

**FIGURE 6** Unprocessed (i)-(iii) and background-subtracted (iv) and (v) surface-enhanced Raman spectroscopy (SERS) signals of trinitrotoluene (TNT) obtained by drying 1 μL of different concentrations of TNT solution on plasmonic superhydrophobic (SHP) needles coated with two-dimensional (2-D) arrays of polyvinylpyrrolidone (PVP)-capped Ag nanocubes.

4 | CONCLUSION

SHP needles with hydrophilic tips are a very simple and effective method of handling and analyzing liquid droplets with volumes ca. ≤ 1 μL with no special equipment or tools. Here, we have shown that this convenience can be combined with the additional sensitivity of SERS by preparing SHP needles where the hydrophilic tips are precoated with a layer of SERS-active Ag or Au nanoparticles. This coating step is conveniently carried out by pushing the tips through a layer of the nanoparticles confined at a water–oil interface, which results in deposition of a monolayer of nanoparticles on the surface. In order to retain the SERS activity during the deposition step, the particles are capped with PVP to prevent them from jamming together as they are deposited from a shrinking interface onto the surface. In use, small (microliter) droplets are applied to the tip of the plasmonic SHP needles where they are pinned in place and evaporate, leaving a solid deposit in contact with the enhancing layer which can then be Raman probed. The dual enhancement mechanism which combines physical analyte enrichment and plasmonic enhancement allows extremely small amounts of sample to be detected with ease on plasmonic SHP needles. In the current work, the detection limit of the CV test sample was 2 pg, whereas that for TNT was 2.5 ng.