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Chemically Stable Au Nanorods as Probes for Sensitive Surface Enhanced Scattering (SERS) Analysis of Blue BIC Ballpoint Pens

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Abstract. Au nanorods were used as an alternative to commonly used Ag nanoparticles as Surface Enhanced Raman Scattering (SERS) probes for identification of dye composition of blue BIC ballpoint pens. When used in combination with Thin Layer Chromatography (TLC), Au nanorod colloids allowed identification of the major dye components of the BIC pen ink, otherwise not identifiable by normal Raman spectroscopy. Thanks to their enhanced chemical stability compared to Ag colloids, Au nanorods provided stable and reproducible SERS signals and allowed easy identification of phthalocyanine and triarylene dyes in the pen ink mixture. These findings were supported by FTIR and MALDI analyses, also performed on the pen ink. Furthermore, the self-assembly of Au nanorods into large area ordered superstructures allowed identification of BIC pen traces. SERS spectra of good intensity and high reproducibility were obtained using Au nanorod vertical arrays, due to the high density of hot spots and morphological reproducibility of these superstructures. These results open the way to the employment of SERS for fast screening analysis and for quantitative analysis of pens and faded pens which are relevant for the fields of forensic and art conservation sciences.

INTRODUCTION

The analysis of commercial ballpoint pens towards the identification of ink composition has been the object of forensic investigation for many years. However, this field of research is also increasingly becoming relevant for art conservation applications. In fact in the last 80 years artists have used ballpoint pens for the production of artworks nowadays found in many museum collections all over the world. Unfortunately, such artworks are rapidly deteriorating due to the fast color fading caused by exposure of the ink to light and air. The answer to this problem requires the establishment of novel long-term preservation approaches which in turn can only be developed if the chemical composition of fading dyes and their interaction with light are well-known and understood.

Ballpoint pen inks are complex mixtures of several dyes and pigments constituting up to 50% of the total ink formulation contained in either a glycol-based solvent or benzyl alcohol.[1-2] Additional components (vehicle) include fatty acids, softeners and polymeric resins, designed to improve the consistency, flow or drying characteristics of the ink.[3] Many analytical methods, including chromatographic techniques[4-7] and mass spectrometry,[8-9] have been used for investigation of ink composition in the field of forensic analysis, mainly aiming at development of reliable protocols towards the establishment of the source or authenticity of a questioned document. Recently, preference has been given to spectroscopic techniques such as Fourier transform infrared (FTIR),[10-11] X-ray fluorescence,[12] Raman spectroscopy[13] due to their inherent non-destructive nature. In fact, spectroscopic techniques require a small amount of analyte, little or no manipulation of the specimen, are simple to perform and therefore allow preservation of the integrity of the analyzed object, which is a strong requisite for both forensic and art conservation applications. Among spectroscopic techniques, Surface Enhanced Raman Scattering (SERS) has been recently successfully

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applied to the analysis of inks, where strong Raman signals were obtained, due to the ability of SERS to quench the fluorescence interference associated with Raman measurements. One of the most comprehensive studies in this field was performed by Geiman *et al.* who analyzed the discrimination capabilities of SERS with various excitation wavelengths[14]. They found that while under normal Raman conditions only FT-Raman excitation provided good spectra, SERS spectra were obtained using diluted solutions of all dye molecules at 633 nm and 785 nm excitation wavelengths. Seifar *et al.* also tested the applicability of SERS for the discrimination of blue and back ballpoint pens and concluded that illumination at 685 nm was necessary for the spectra to be distinguished[15]. The authors also reported poor reproducibility due to the fast oxidation of Ag colloids used as SERS probes and the contribution from the laser which caused burning of the sample. In contrast, White *et al.* reported stability of results with the use of Ag colloids, attributed to the order in which the colloidal solution and the aggregating agent poly-L-lysine was added, as well as the use of a fine nib ensuring homogenous distribution of the colloid on the paper.[16] Overall, the reports on the SERS performance of Ag colloids were contrasting with the additional following drawbacks reported: measurements had to be performed within minutes of colloid deposition due to fast Ag oxidation, SERS signals were not reproducible due to inhomogeneous (coffee stain effect) evaporation of deposited colloidal solutions, charged polymers had to be added to induce SERS effects between negatively charged Ag colloids and negatively charged dyes. In spite of this, reports on the use of alternative, more chemically stable SERS probes for ink identification are scarce[17].

Recently, theoretical work by Hao *et al.* calculated that Au nanorods provide the greatest SERS enhancements compared to other nanoparticle shapes, due to the high density of electric-field concentrated at their tips[18]. In addition, the SERS abilities of chemically stable ordered Au nanorod arrays were investigated by our group. The arrays displayed enhancement factors (EFs) up to 10^5, a factor higher than spherical Au particles and comparable to EFs displayed by Ag nanoparticles, without the drawback of fast degradation by oxidation displayed by Ag nanoparticles[19, 20].

In this paper we .report on the use of chemically stable Au nanorod colloids and arrays for SERS analysis of a blue ballpoint BIC pen. Au nanorods were used as suspension and in combination with Thin Layer Chromatography (TLC) to identify the dye components of the BIC pen. While normal Raman conditions did not allow identification of specimens separated by TLC, SERS was successful in obtaining enhanced spectra for all TLC coloured spots. High intensity and good signal-to-noise SERS spectra were obtained, due to the matching of the laser illumination with the plasmon resonance of the used nanorods. In contrast with what reported in literature, Au nanorods gave stable SERS signals for weeks after deposition and could be used without the need of additional aggregating agents. The SERS analysis allowed the identification of Blue 38 and Crystal Violet in the dye mixture, which was also confirmed by FTIR and MALDI analysis. In addition, Au nanorod arrays were used to obtain sensitive spectra of BIC pen traces otherwise not observable under normal Raman conditions. The high degree of order and the high density of hot spots in the arrays enabled the detection of SERS spectra with high reproducibility from MeOH extracts of concentration < 100 nM.

EXPERIMENTAL SECTION

Materials. Tetrachloroauric acid, silver nitrate, sodium borohydride, ascorbic acid, cetyltrimethyl-ammoniumbromide (CTAB), MeOH were purchased from Sigma-Aldrich. All glassware was cleaned with aqua regia prior to nanoink synthesis. Milli-Q water (resistivity > 18 MΩ cm^{-1}) was used throughout the experiments. Reference dyes Blue 38 and Crystal Violet (CV) were also purchased from Sigma and used without further purification.

Synthesis of SERS probes. Au nanorods were synthesized by seed mediated growth reported by Nikoobakht *et al.*[21]. Au nanorod arrays were fabricated as already described in details elsewhere[19, 20].

Scanning electron microscopy (SEM) images of nanoinks deposited on SiO_2 substrates were acquired using a field emission SEM (JSM-6700F, JEOL UK Ltd.) operating at beam voltages of 2 kV.

Thin Layer Chromatography was performed with 5×10 cm silica plates (Sigma-Aldrich). The BIC ballpoint pen was deposited on the TLC by directly drawing lines on the plate whereas the reference samples were deposited as MeOH solutions (5 μl, 3 mM). TLC plates were developed in acetone: H_2O 2:1 (v/v) for 30 min.

HR MALDI mass spectra were recorded on a FT-ICR mass spectrometer (Bruker) equipped with a 7T magnet. The samples were ionized in positive ion mode using the MALDI ion source. Samples were prepared by extracting 0.1 g of the matrix (from ballpoint pen end-tips) with 1.0 mL of methanol (HPLC grade) for 30 minutes.

Optical characterization*:* UV-Vis spectra were acquired with an Agilent/HP 8453 UV-Vis Spectrophotometer (200nm < λ < 1100nm). Raman spectra at 514 nm were obtained from a Renishaw inViaRaman system. A helium-neon laser was employed as an excitation source. The laser beam was focused onto the sample through a Leica 20X objective with 0.4 N.A. Measured power at the sampling level was controlled at about 3 mW. Acquisition time was usually 10 s. Raman spectra at 785 nm were obtained from a Perkin Elmer Raman station. The laser beam was focused onto the sample through a 50X objective (M Plan Achromat) with 0.75 N.A. The laser power was around 35 mW and typical acquisition time was 10 s. To obtain SERS spectra, 5 μL of Au nanorods were deposited on the TLC plate and left to evaporate over 10 minutes. Alternatively, 5 μL of BIC MeOH solution were deposited on Au nanorod arrays and left to evaporate. FTIR spectra were taken with a Vio-Red Merlin FTIR instrument. Samples were prepared by immersion of the ballpoint pen end-tip in MeOH. Reference samples were obtained by dissolving solid dyes in MeOH (1 mM). Prepared solutions were deposited on CaF_2 plates and left to dry before analysis.

RESULTS AND DISCUSSION

Figure 1a displays a photograph of a TLC plate showing separation of the BIC pen dye components obtained by using an acetone: H2O 2:1 (v/v) eluent. As result of ink mixture separation the TLC displayed a blue spot and a purple spot with retention factors (Rf) equal to = 1 and 0.62, respectively. For comparison reference dyes solvent Blue 38 and CV (see formulas in Figure 1 b,c) were also deposited on the TLC and run alongside the pen spot. These dyes were specifically selected as triarylene dyes and phthalocyanine pigments were identified in the literature as components of the BIC ballpoint blue pen.22,15 Deposited Blue 38 displayed a retention factor (Rf) equal to = 1, whereas CV displayed Rf equal to = 0.62, equivalent to the Rfs of the BIC blue and purple spots, respectively.

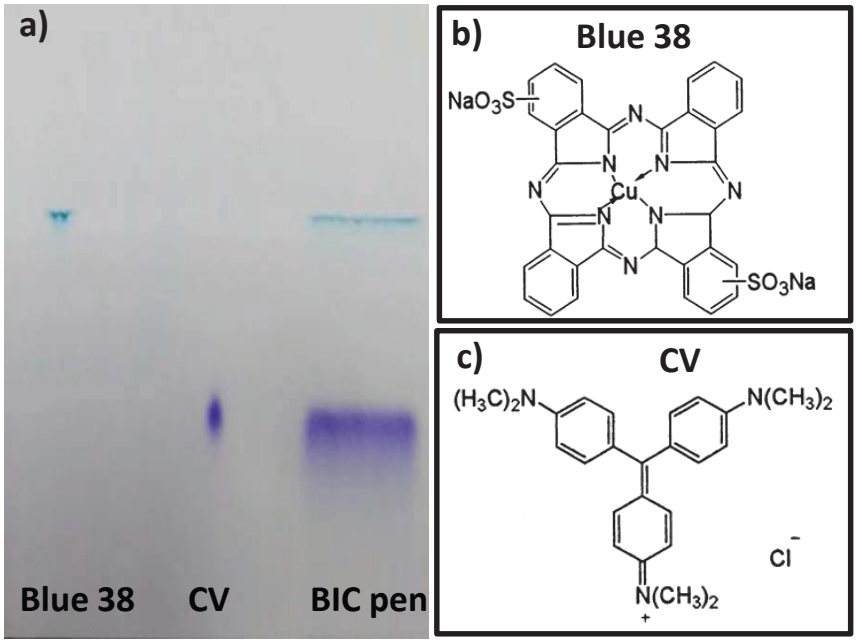


FIGURE 1. (a) Photograph of a TLC plate showing BIC pen components and reference samples Blue 38 and CV. Eluent acetone:H2O 2:1 (v/v); (b, c) molecular formulas of reference samples Blue 38 and CV.

In order to verify the presence of the above reference dyes in the pen ink mixture, Normal Raman (NR) measurements were performed directly on the TLC colored spots at excitation wavelength 785 nm. The blue spot

and Blue 38 specimens displayed good spectra (Figure 2a light and dark blue curves, respectively) characterized by the same diagnostic peaks at 1539 cm^{-1}, 1340 cm^{-1} and 720 cm^{-1} associated with internal vibrations of the phthalocyanine macrocycle [23,24]. In contrast, the spectrum of the purple spot (Figure 2a, light purple curve) displayed no features and the spectrum of the reference CV (Figure 2a, dark purple curve) displayed only small peaks around 1600 cm^{-1}. From these data it was possible to preliminary identify the BIC pen blue spot as Blue 38 but no correlation between the BIC pen purple spot and CV could be made due to the featureless spectra obtained under NR conditions. Figure 2b shows the SERS spectra of an equivalent TLC where Au nanorods were deposited (after TLC running) in all spots previous to illumination with 785 nm excitation. The spectra of the blue specimens, already visible under NR conditions, appeared slightly enhanced and showed peaks equivalent to those recorded under NR conditions. In contrast, the purple spot and CV showed highly enhanced spectra compared to NR conditions. Both spectra displayed the same diagnostic peaks at 1620 cm^{-1}, 1592 cm^{-1}, 1540 cm^{-1}, associated to stretching of the benzene rings and 439 cm^{-1} and 420 cm^{-1} associated with bending of the CNC bonds.[25]

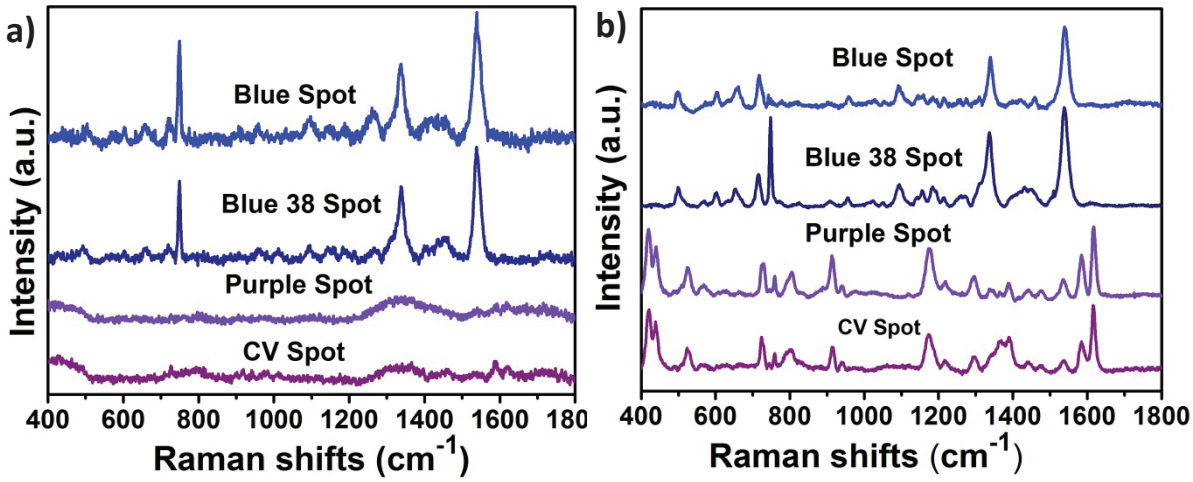


FIGURE 2. (a) Normal Raman (NR) and (b) SERS spectra of TLC Bic pen components and reference samples Blue 38 and CV taken at illumination wavelength 785 nm.

It should be clarified that SERS spectra taken in different locations of the same TLC spot showed high peak position reproducibility, which was indispensable for the attribution of sample identity. However, the spectral intensity was not reproducible (standard deviation of 60 % between SERS measurements taken at different locations within the same spot). This can be clearly explained by observation of the SEM images reported below (Figure 3) depicting nanoords deposited on TLC plates. The granular morphology of the TLC plates combined with the random formation of nanorod aggregates driven by solvent evaporation, resulted in SERS spectra of poor reproducibility. The high intensity and good quality of spectra obtained by SERS analysis allowed to undoubtedly associate the BIC pen blue spot to Blue 38 and the BIC pen purple spot to CV and therefore provided a fast and sensitive analytical tool for the identification of Blue 38 and CV as BIC pen ink components. In addition, when Au nanorods were used as SERS probes none of the instability problems associated with the use of Ag colloids reported by other authors were observed. Au nanorods were chemically stable and TLC separated plates could be illuminated after weeks of nanorods deposition provided that the TLC was stored in the dark in order to prevent ink color fading. Furthermore, no use of aggregating agents was necessary and no adjustment of electrostatic charge had to be made to promote chemical link with charged analytes (i.e. between positively charged Au nanorods and positively charged CV).

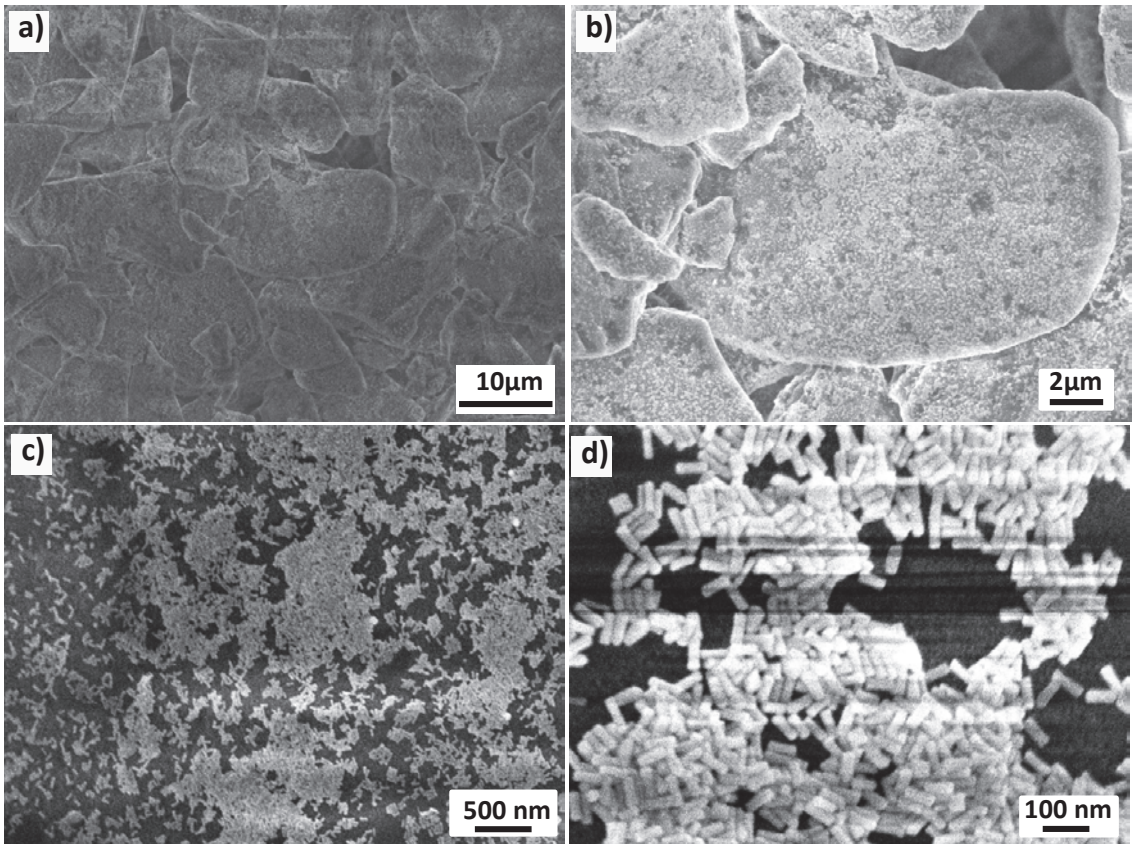


FIGURE 3. SEM images of Au nanorods deposited on TLC plates ranging from lowest (a) to highest (d) magnification.

The origin of the strong enhancement was ascribed with the use of a laser illumination in resonance with the longitudinal plasmonic peak of the Au nanorods. This is clearly shown in Figure 4 where the UV-vis spectrum of the Au nanorod aqueous suspension used as SERS probe along with the absorption spectra of the reference dyes are reported. Such resonant conditions provided the necessary electromagnetic enhancement enabling visualization of spectra otherwise not observable under NR conditions.

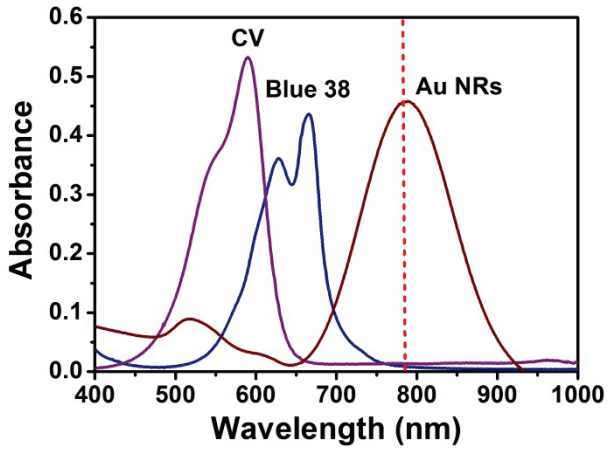


FIGURE 4. UV-vis spectra of reference dyes Blue 38 and CV in MeOH and Au nanorods aqueous suspensions. Red dotted line shows the wavelength position used for NR and SERS illumination (785 nm).

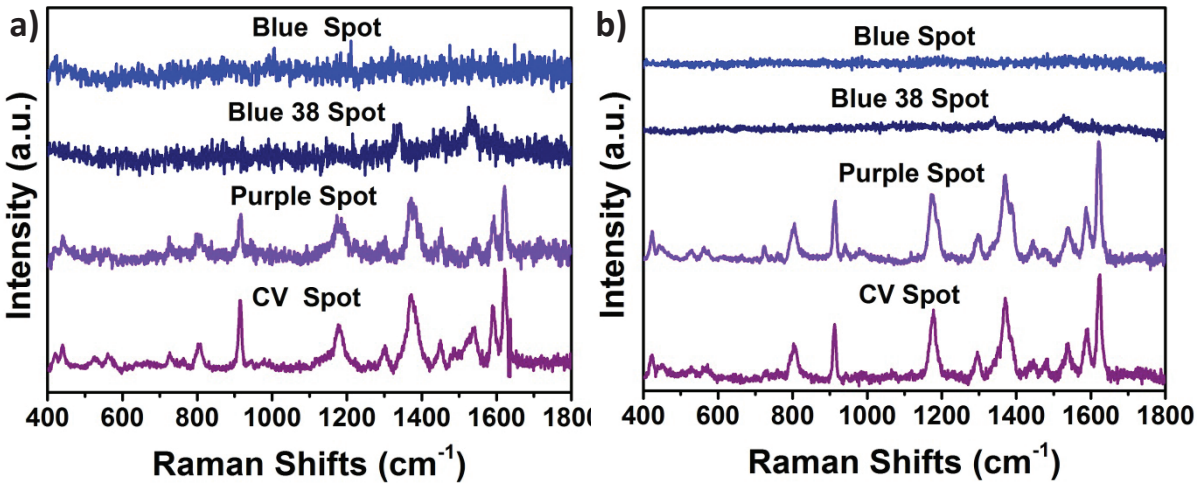


FIGURE 5. (a) Normal Raman (NR) and (b) SERS spectra of TLC BIC pen components and reference samples Blue 38 and CV taken at illumination wavelength 514 nm.

In order to prove that the observed enhancement was associated to the use of nanorods in resonant conditions, NR and SERS spectra were also taken with 514 nm excitation illumination. The NR spectrum of the blue spot (Figure 5a, light blue curve) appeared featureless. A low intensity spectrum was also obtained for Blue 38 with only two peaks appearing at 1539 cm^{-1} and 1337 cm^{-1} (Figure 5a, dark blue curve). In contrast, spectra of relatively good intensity were obtained for the purple spot and CV with features analogues to the ones obtained for SERS illumination at 785 nm. The appearance of these spectra was likely due to the use of an excitation wavelength in molecular resonance with CV (see Figure 4). SERS spectra were also recorded at 514 nm, after deposition of Au nanorod colloids to all separated spots (Figure 5b). However SERS spectra displayed features equivalent to the NR spectra recorded at 514 nm, sign that no SERS effect occurred due to the absence of plasmonic resonance conditions.

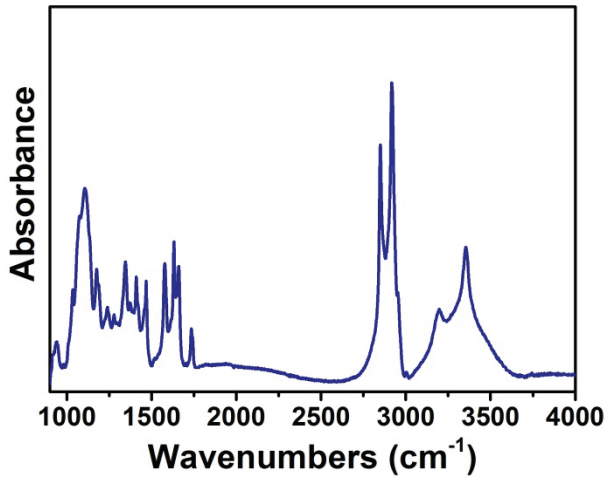


FIGURE 6. FTIR spectrum of BIC pen MeOH solution.

FTIR analysis of the blue BIC pen ink gave some useful and complementary information about the ink composition and confirmed the presence of some specific dyes in the formulation. The FTIR spectrum is reported in Figure 6. The peaks at 1577, 1374, 1175 and 939 cm^{-1} were diagnostic of the presence of triarylmethane dyes, in this case CV, and confirmed the findings of the SERS analysis [26]. In addition, FTIR analysis revealed the presence of Acid Blue 9 in the ink formulation. Additional information about the presence of other non-dye components not obtainable by SERS was also obtained. The carbonyl absorption band at 1735 cm^{-1} and the carboxylate group stretching at 1408 cm^{-1} suggested the presence of an acrylic-based emulsion [27], whereas the presence of the amide vibration at 1656 cm^{-1} suggested the presence of an unidentifiable amide-based compound, possibly deriving from

acrylamide based resins [28,29]. The presence of some asymmetrical and symmetrical stretch vibrations of the CO single bonds at 1278, 1075 and 939 cm^{-1} (overlapping the peak at 939 cm^{-1} for the ρ(CH3)/νCN) vibration of CV) suggested the presence aliphatic glycol ethers, usually found in ballpoint pen ink formulations[30]. MALDI analysis (data not shown) confirmed the presence of crystal violet, for the presence of the strong peak at 372 m/z, and also indicated the possible presence of Basic Yellow 2 (Auramine), a common yellow dye usually found in blue inks formulations[31,32], as suggested by detection of the peak at 268 m/z.

Finally, Figure 7 shows the use of highly ordered Au nanorod arrays for sensitive SERS analysis of BIC ballpoint pen traces. The use of ordered nanoscale arrays is highly desirable for SERS analysis as it provides high sensitivity due to the high density of hot spots between closely arranged nanoparticles and also reproducibility of analysis, due to the homogeneity and reproducibility of the SERS substrate. Figure 6a shows a SEM image of the Au nanorod arrays assembled on SiO_2 substrates and stamp-transferred on glass coverslip following a methodology developed by our research group and described in details elsewhere [19,20]. The average size was found 10×41 nm (aspect ratio 4.1) and was calculated from 100 statistical measurements of nanorods taken from high magnification SEM images. The arrays were characterized by large domains (> 100 μm^2) of vertically aligned nanorods with a high density of hot spots. Figure 6b shows the NR and SERS spectra of a MeOH solution of BIC pen drop-deposited on a glass coverslip and on the Au arrays, respectively. The illumination wavelength was 514 nm. The estimated concentration of the solution (from UV-vis measurements) was < 100 nM. While the NR spectrum was featureless, the SERS spectrum was characterized by intense peaks mainly associated to the CV component. The contribution of the Blue 38 component was less evident. This could be associated with a higher concentration of CV in the ink mixture. The high intensity of the peaks suggests that lower concentrations could be detected by using these arrays, which would enable the analysis of pen traces or faded pen traces extremely useful for forensic or art applications. Figure 6c shows spectra of the drop-deposited BIC pen measured in 10 different locations over an array of 5 mm in diameter. The intensity change of the Raman band at 1175 cm^{-1} was used to calculate the relative standard deviation of the intensity from 10 points. A value of 8% was obtained, which showed the remarkable good uniformity of the array. This value was lower than reproducibility values reported in literature for nanoparticle aggregates and printed nanoparticle arrays and they were comparable to values reported for ordered nanowire arrays obtained by nanosphere lithography.[33-35]

A further evaluation of SERS performances of used SERS probes (colloids and arrays) was achieved by calculating the Enhancement Factor (EF), defined as the ratios of the intensities of the scattered radiation for SERS and normal Raman scattering per molecule

$$(1) \qquad EF = (I_{SERS}/N_{SERS})/(I_{NR}/N_{NR})$$

Where, in the case of Au colloids, ISERS and INR are the integrated intensities of the SERS and normal Raman scattering spectra for blue and purple spots on the TLC; NSERS and NNR are the number of molecules found in the laser excitation area adsorbed on Au nanorods and on TLC, respectively. The calculated EFs were 2×104 and 9×104 for the blue spot and the purple spot, respectively [19,36]. No enhancement was obtained with Au nanorods under 514 nm illumination.

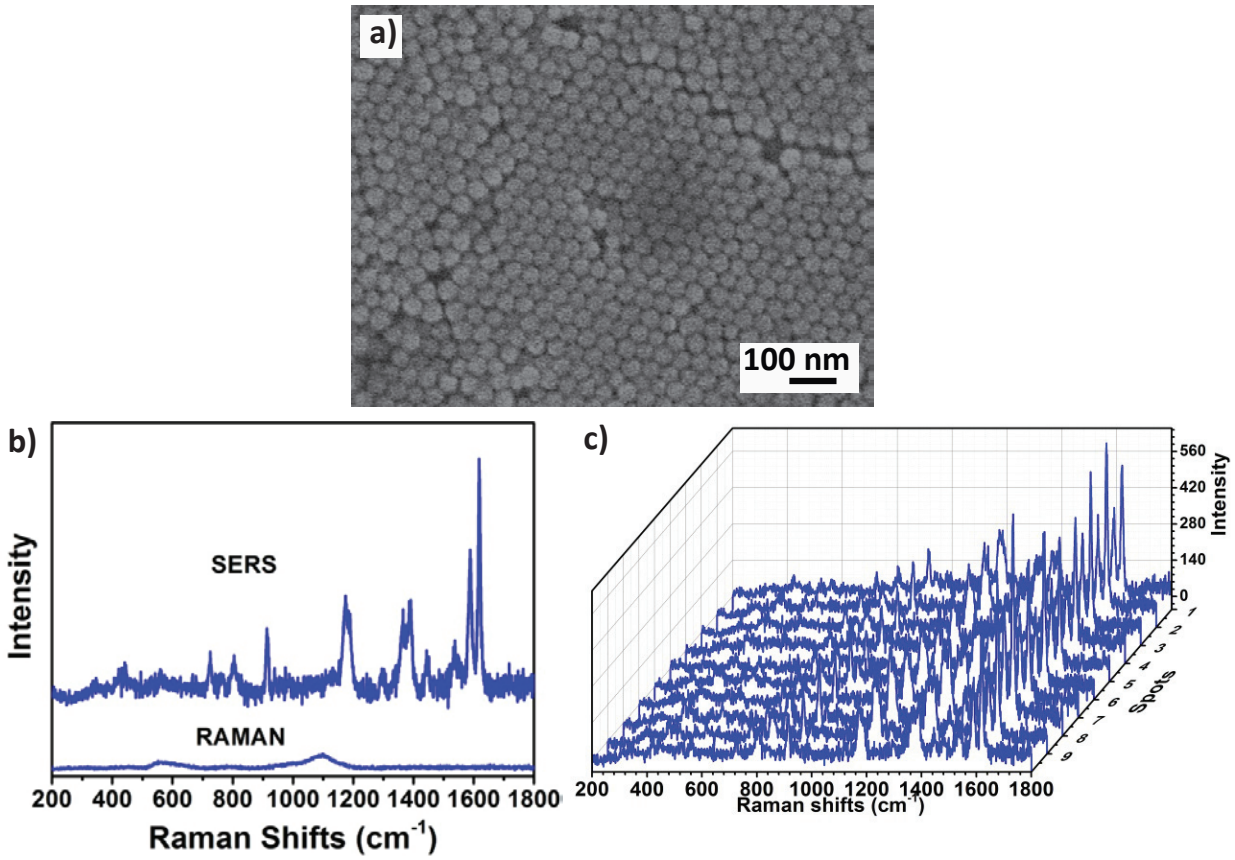


FIGURE 7. (a) SEM image of vertical Au nanorod arrays stamped on a glass substrate; (b) SERS and NR spectra of low concentration BIC pen MeOH solutions; (c) reproducible SERS spectra recorded at 10 different locations of a 5 mm diameter Au nanorod array.

Regarding Au nanorod arrays, I_{SERS} and I_{NR} are the integrated intensities of the SERS and normal Raman scattering spectra for the BIC pen (calculated assuming that the main dye content of the BIC was constituted by CV); N_{SERS} and N_{NR} are the number of molecules found in the laser excitation area. The calculated EF was 1×10^5, in agreement with values already reported for these superstructures[19].

CONCLUSIONS

In conclusion, we have shown the use of Au nanorods as efficient and chemically stable SERS probes for sensitive analysis of ballpoint BIC pens. Au nanorod colloidal solutions were used in combination with TLC, providing clear and enhanced spectra for all pen components, otherwise not discernible under NR conditions. The observed SERS enhancement was attributed to the use of a laser illumination in plasmonic resonance with the Au nanorod probes. Phthalocyanine Blue 38 and tryarylene CV were identified in the dye mixture of the BIC pen. These findings were confirmed by FTIR and MALDI analysis. The SERS probes used were chemically stable, did not necessitate the addition of aggregating or binding agents, and could be used for days after deposition. Furthermore, the use of Au nanorod arrays carrying a high density of hot spots provided the enhancement necessary to enable detection of BIC pen traces with a high level of uniformity. The developed probes offer an alternative to existing analytical tools for the reliable, fast and low cost analysis of ballpoint pens and concomitantly open the way to the analysis of trace amounts particularly relevant for forensic and art applications. The use of SERS probes with reproducible features also potentially enables quantitative analysis, a highly desirable feature that has the potential to enhance the analytical capabilities SERS to a degree comparable to chromatographic methods.

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