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Fabrication of highly active and cost effective SERS plasmonic substrates by electrophoretic deposition of gold nanoparticles on a DVD template

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ABSTRACT

In this work we present a simple, rapid and cost effective method to fabricate highly active SERS substrates. This method consists in an electrophoretic deposition of gold nanoparticles on a metallic nanostructured template of a commercial digital versatile disk (DVD). The negatively charged gold nanoparticles self-assemble on the positively charged DVD metallic film connected to a positive terminal of a battery, due to the influence of the electric field. When gold nanoparticles self-assembled on DVD metallic film, a 10-fold additional enhancement of Raman signal was observed when compared with the case of GNPs self-assembled on a polycarbonate DVD substrate only. Finite-difference time-domain simulations demonstrated that the additional electromagnetic field arising in the hot-spots created between gold nanoparticles and DVD metallic film induces an additional enhancement of the Raman signal. SERS efficiency of the fabricated plasmonic substrate was successfully demonstrated through detection of para-aminothiophenol molecule with three different excitation laser lines (532, 633 and 785 nm). The enhancement factor was calculated to be 10^6 and indicates that plasmonic substrates fabricated through this method could be a promising platform for future SERS based sensors.

1. Introduction

Recently, there has been growing interest in developing sensing applications based on Surface Enhanced Raman Spectroscopy (SERS) in medicine and life sciences, environmental science, agriculture and food production, forensic, etc. [1–6]. SERS is a very sensitive and powerful technique that allows the detection of ultra-low concentration of analytes using the amplification of electromagnetic field generated by the excitation of localized surface plasmons. SERS enhancement originates from a combination of chemical and electromagnetic mechanisms [7]. The chemical mechanism is related to the chemisorbtion of analyte molecules to a noble metal surface that allows the transfer of electrons both from the analyte molecules to the metal and from the metal to the analyte molecules. The electromagnetic mechanism is related to the excitation of the localized plasmonic resonance and leads to the enhancement of the incident electromagnetic field intensity by 10^4 folds [8]. Such enhancement is possible when light interacts with noble-metal nanostructures and a strong localized electromagnetic field is generated due to the surface plasmon resonance [9,10].

The number of SERS-active substrates proposed in the last few years is continuously increasing. This is due to the development of a variety of fabrication approaches ranging from electron beam lithography [11], nano-imprinting [12], self-assembly of metallic nanoparticles [13,14], deep UV lithography [15,16], electrophoresis attachment of metallic nanoparticles [17] to deposition of metallic films over structured nanospheres [18], etc. Because fabrication of SERS substrates by electron beam lithography and nano-imprinting is rather complex and expensive (also limiting the number of SERS applications), other preparation methods implying low cost, reproducibility, efficiency and stability that could be implemented on large scale SERS applications, need to be developed. For example, recently, commercial cost-effective and widely accessible compact disks (CDs) and digital versatile disks (DVDs) were used in various sensing applications. For instance, CD substrates have been implemented as effective electrodes for electro analytical chemistry and biomedical sensors [19,20] while DVD-derived corrugated templates have been used not only to grow self-organized colloidal crystals [21] but also as matrices for the fabrication of nanostructures for further use in plasmonic applications [22].

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Here, we present a simple, rapid and cost effective method to fabricate highly active SERS substrates by an electrophoretic deposition of gold nanoparticles (GNPs) on a metallic nanostructured template that is obtained by mechanical processing of a commercial DVD. Using this active plasmonic substrate, SERS spectra of para-aminothiophenol (p-ATP) molecules were successfully recorded with three different excitation laser lines (532, 633 and 785 nm). This proves that such plasmonic substrates are active over a large excitation wavelength domain. Furthermore, finite-difference time-domain (FDTD) calculations showed that the electromagnetic field is highly amplified by the strong coupling between both neighboring GNPs and between GNPs and the DVD metallic film. Such resulting plasmonic substrate (GNPs on DVD; hereafter simply GNPs@DVD) generates both a significant SERS enhancement (enhancement factor EF = 10^6) and a 10-fold increased SERS signal when compared to a SERS substrate realized by simply drop casting GNPs on the polycarbonate side of the DVD. Moreover, when a laser excitation wavelength of 785 nm is used, an extra field enhancement can be generated in the textured DVD metallic film due to the excitation of propagative surface plasmons.

2. Experimental

2.1. Chemicals and reagents

$HAuCl_4 \cdot 3H_2O$ and para-aminothiophenol (p-ATP) were purchased from Sigma Aldrich and used as received. DVDs (4.7 GB) were purchased from commercial sources. Deionised water (DI) was used for preparation of solutions and rinsing procedures. A 9 V commercial battery (GP Power Cell) was used as an electrical source.

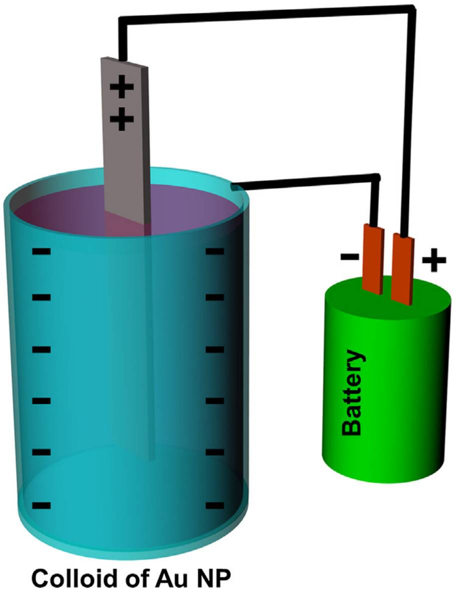
2.2. Synthesis of gold nanoparticles

GNPs were synthesized using the standard reduction of $HAuCl_4$ with trisodium citrate, also known as the Turkevich-Frens method [23]. Briefly, 100 mL of $HAuCl_4 \cdot 3H_2O$ solution, with a concentration of 10^{-3} M were heated until the boiling point was reached. Then, quickly, 10 ml of 38.8×10^{-3} M sodium citrate were added while stirring vigorously. After that, the boiling process was maintained until the color of the mixture changed from yellow to intense burgundy-red. The solution was then removed from the heater and cooled at room temperature, while the stirring process was still sustained for another 15 min.

2.3. Preparation of GNP@DVD substrate

In order to fabricate the SERS plasmonic substrate, we used a commercial DVD that was cut in small pieces. One such piece was further split and the resulting polycarbonate part holding de metallic film was firstly rinsed in methanol in order to remove the photosensitive dye from the surface, followed by subsequently rinsing in DI water in order to remove the remaining methanol and the dissolved dye from the metallic surface. At the end, the DVD metallic film was dried in a Rypa oven. Once dried, the DVD metallic film was further used for the electrophoretic deposition of the synthesized GNPs. For that, a home-made electrophoretic depositing device, comprised of a battery (9 V) and two electrodes, was used (Scheme 1).

A cylindrical container from aluminum foil was used as the anode. The aluminum container was filled with the colloidal solution of GNPs. Because the Zeta potential of GNPs is negative, the nanoparticles are rejected by the aluminum container walls. A DVD metallic film of a rectangular shape was then attached to the positive terminal of the battery and used as the cathode. Once the cathode is immersed in the colloidal solution, negatively charged GNPs are attracted by the DVD metallic film. This way, the GNPs start to self-assemble on the DVD metallic film forming the GNP@DVD. Note that, in order to achieve uniform self-assembling of GNPs on the DVD metallic film, we used the optimal immersion time of the cathode of about 15 s.



Scheme 1. Home-made device used for electrophoretic deposition of GNPs on the DVD metallic film.

2.4. Preparation of samples for SERS investigation and measurements

To measure the SERS efficiency of the obtained GNP@DVD substrate, we have prepared a methanol solution of p-ATP (10^{-4} M) and immersed the GNP@DVD substrate in this solution for 24 h. After that, the substrate was well rinsed in methanol (in order to remove any non-adsorbed p-ATP molecules) and in water, followed by drying at room temperature for 30 min.

The morphology of the DVD metallic film and GNP@DVD substrate was analyzed using a Witec Alpha 300 A atomic force microscope (AFM) in contact mode. Particle size distribution and zeta potential were measured by a Zetasizer NanoZS90 instrument (Malvern Instruments). Raman signal was recorder in backscattering geometry with a Witec Alpha 300R Confocal Raman Microscope equipped with a Raman Spectroscopy System UHTS 300 charge coupled device operating at −60 °C, using 532, 633 and 785 nm lasers as excitation sources. Raman signal was collected through a confocal pinhole of 100 μm diameter by using a 0.9 numerical aperture (NA) objective of 100x magnification.

3. Results and discussion

3.1. Characterization of gold nanoparticles

GNPs were initially investigated by UV–vis spectroscopy. The extinction spectrum presented in Fig. 1(a) emphasizes a plasmonic band at 520 nm which can be attributed, according to the literature, to spherical nanoparticles with a diameter of 15–22 nm [24]. The diameter of GNPs was also determined from the dynamic light scattering (DLS) measurement presented in Fig. 1(b). These results are consistent with the UV–vis measurements and the literature [24]. From Zeta potential measurement presented in Fig. 1(c) we deduced a Zeta potential for the GNPs of about −37 mV. This potential is providing enough electrostatic repulsion between