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ENGINEERED PAPER PLATFORM LOADED WITH GOLD NANOSPHERES TO IMPROVE SERS PERFORMANCE FOR ANALYTE DETECTION

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ABSTRACT. In this paper, we report a flexible surface enhanced Raman scattering (SERS) nanoplatform based on a Whatman paper loaded with gold nanospheres *via* a direct immersion approach. After the fabrication and optical/morphological characterization, the SERS performance of our plasmonic nanoplatforms was tested using the non-resonant Raman p-aminothiophenol (p-ATP) analyte. Finally, the plasmonic nanoplatform developed here has demonstrated to have excellent reproducibility, the SERS efficiency being highly dependent on the AuNPs concentration loaded on the 3D flexible scaffold paper.

Keywords: *paper substrate; gold nanospheres; SERS detection, sensor nanoplatform*

INTRODUCTION

In the recent years, a growing interest is focused on the possibility to fabricate efficient, stable, reproductible and inexpensive bio(nano)sensors

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that can be effectively implemented in the clinical analyses in order to identify various diseases in their early stages, hence preventing their progression [1].

Paper has recently been claimed as an ideal flexible substrate for inexpensive analytical tests both in health and environment applications [2]. Although enzyme-linked immunosorbent assay (ELISA) -as a common solution-based tool- can be theoretically applied to paper, it requires multiple reactants as well as washing steps, making this technique complicated and hard to implement [3]. Therefore, a direct technique able to detect analytes of interest even at very low concentrations, through the direct interaction between the treated paper substrate and analytes, is highly desired. Surface-enhanced Raman scattering (SERS) can be such a technique, by combining the molecular specificity of the Raman spectroscopy with the high sensitivity of the gold nanoparticles based on their exceptional plasmonic properties (i.e. field enhancement) [4]. In this context, the SERS technique is continuously applied in food, water or clinical analysis, major research topics, which are associated with a healthy life style aiming to prevent diseases. Even so, for the direct implementation of the plasmonic platform in routine SERS applications, it is a critical requirement to engineer robust, reproductible, stable and sensitive substrate. Paper, with its excellent features such as easy-to-use, flexibility, robustness, three-dimensional (3D) porosity and so on, represents -therefore- a promising SERS nanoplatform for different relevant bioassays [5,6] .

In this paper, positively charged cetyltrimethylammonium chloride (CTAC) spherical nanoparticles (denoted further as CTAC@AuNPs) in solution were loaded via a simple immersion approach onto the Whatman no 1 paper, selected herein as common filter paper consisting of 98 % α-cellulose. We proved that after the CTAC@AuNPs loading on paper, their characteristic optical response in aqueous solution was well-transferred and maintained on the paper substrate. The CTAC@AuNPs size and morphology of the as-fabricated plasmonic paper substrate were rigorously characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively. Then, a model Raman analyte, p-aminothiophenol (p-ATP), was adsorbed on the CTAC@AuNPs paper substrate and its generated SERS signal was evaluated.

Further on, the effect of the CTAC@AuNPs concentration loaded on the paper - induced and controlled by three successive dipping steps- was finally discussed in terms of SERS performance of our engineered paper nanoplatforms, in the context of the increased necessity to improve the paper-based SERS nanoplaforms efficiency for further specific biodetection.

EXPERIMENTAL DETAILS

Chemicals

Hydrogen tetrachloroaurate-(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.99 %), sodium borohydride ($NaBH_4$), Hexadecyltrimethylammonium bromide (CTAB, 96%), Cetyltrimethylammonium chloride solution (CTAC), ascorbic acid (AA), p-aminothiophenol (p-ATP) and Whatman® qualitative filter paper, Grade 1 (Whatman no. 1) were purchased from Sigma-Aldrich (Germany). All chemicals were of analytical grade, and all aqueous solutions were prepared using ultrapure water (resistivity ~ 18 MΩ).

Synthesis of CTAC-stabilized gold nanospheres

The CTAC-stabilized gold nanospheres (CTAC@AuNPs) were synthesized using an adapted version of the previously reported approach by Zheng *et al*. [7]. In summary, the CTAB-capped Au clusters were firstly prepared by adding a $NaBH_4$ solution to a 10 ml mixture of 0.25 mM $HAuCl_4$ and 100 mM CTAB. 10 µl of Au clusters were then mixed with a freshly prepared solution of 2 ml CTAC (200 mM) and 1.5 ml of AA, followed by the addition of a 2 ml of 0.5 mM $HAuCl_4$ solution in order to finally obtain Au seeds of 10 nm diameter. After 15 min reaction at 27 °C, the seeds were centrifuged once at 14500 rpm for 30 min and redispersed in 1 ml 20 mM CTAC solution.

Fabrication of the plasmonic strips

For the preparation of plasmonic nanoplatforms, paper strips were firstly cut from the Whatman sheet and thenafter immersed into a Petri dish that contained CTAC@AuNRs colloidal solution for 10 minutes and left to dry 10 minutes at 45 ^{o}C before further analysis. In order to increase the CTAC@AuNPs concentration loaded on paper, the immersion procedure was repeated 3 times.

Preparation of SERS active paper nanoplatforms

10 µL ethanolic solution of 10^{-5} M of p-ATP molecules were prepared and dropped onto the dried CTAC@AuNPs paper to create a p-ATP monolayer on the plasmonic nanoplatform.

Experimental measurements

The extinction spectra of the CTAC@AuNPs in aqueous solution and loaded onto the paper substrate were recorded using a Jasco V-670 UV-Vis-NIR spectrophotometer with 1 nm spectral resolution. The morphology of the CTAC@AuNPs was examined using a FEI Tecnai F20 field emission, high resolution TEM (TEM/HRTEM) operating at an accelerating voltage of 200 kV and equipped with Eagle 4k CCD camera. Dynamic light scattering (DLS) and Zeta Potential measurements were performed using a Zetasizer Nano ZS 90 from Malvern Instruments. The morphology and the uniformity of the engineered CTAC@AuNPs nanoplatforms were investigated by scanning electron microscopy (SEM) using a FEI Quanta 3D FEG scanning electron microscope. All SERS spectra were recorded in air using a portable spectrometer (Raman Systems R3000CN) equipped with a 785 nm diode laser coupled to a 100 µm optical fiber.

RESULTS AND DISCUSSION

First, the optical response of the as-prepared CTAC@AuNPs in aqueous solution was investigated and depicted in Fig. 1. As such, the as-synthesized colloidal CTAC@AuNPs exhibit a plasmonic resonance band

centered at 529 nm (Fig. 1), which is consistent with an average diameter of 45±3.5 nm, as provided by transmission electron microscopy (TEM) observation (inset in Fig. 1). The CTAC@AuNPs size investigation by DLS measurement also revealed a highly monodispersed plasmonic AuNPs with an average hydrodynamic diameter of 55 nm (data not shown here). The advantages of employing this seed-mediated growth method is represented by: i) the resulting positively charged CTAC@AuNPs having a zeta potential of + 51 mV, allowing their direct electrostatic interaction with the negatively charged cellulose, caused of its hydroxyl groups [8]; ii) the narrow full width at half maximum (FWHM) compared to the citrate-covered AuNPs synthesized using the well-known standard Turkevich method [9], allowing thus this type of AuNPs to be further implemented as robust LSPR biosensors.

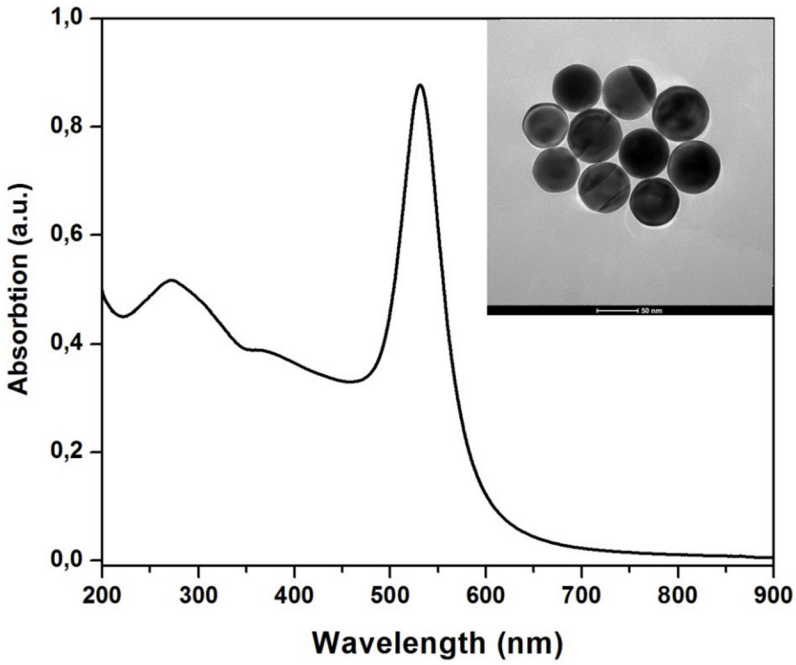

Fig. 1. The extinction spectrum of the CTAC@AuNPs obtained in aqueous solution. In inset is presented a representative TEM image of the synthesized CTAC@AuNPs.

After the immersion of the filter paper into the colloidal solution for 10 minutes, the color of the paper becomes red, in concordance with the color of the colloidal solution, denoting the first prove that the CTAC@AuNPs were successfully loaded onto the paper (Fig. 2(c)). To note that the color intensity of the dried CTAC@AuNPs paper nanoplatform became more intense as the number of the immersion steps was increased. SEM investigation was subsequently employed to confirm the presence of CTAC@AuNPs on the paper substrate in a dense and uniform distribution. As such, Fig. 2(b) depicts a typically SEM image, showing one bare paper microfiber, without CTAC@AuNPs. Contrarily, Fig. 2(b) shows a paper fiber with the loaded CTAC@AuNPs, the nanoparticles being well-adsorbed on paper after their diffusion from the colloidal solution into the 3D porous structure of the Whatman paper.

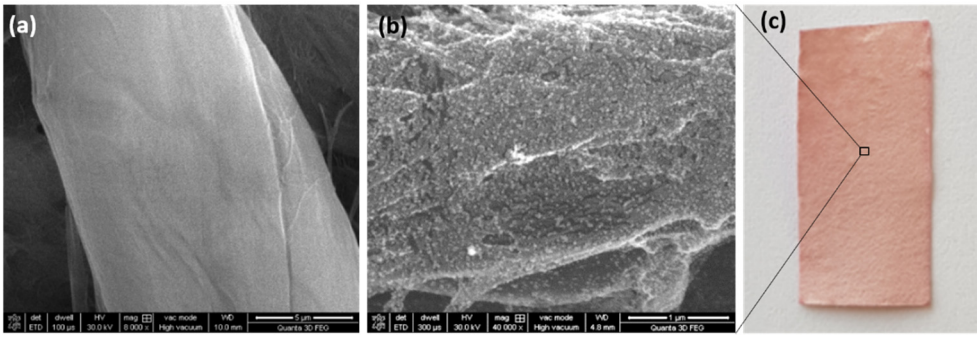

Fig. 2. (a) Representative SEM images before (bare Whatman paper) and (b) after loading with CTAC@AuNPs. (c) Digital photo of the fabricated plasmonic paper.

Further on, the UV-Vis analysis was performed on the fabricated plasmonic-paper nanoplatform. Specifically, the plasmonic response of the CTAC@AuNPs loaded on paper was well-preserved, and -more importantly- the amount of the CTAC@AuNPs adsorbed on the paper micro(nano)fibers increases with the number of immersion steps (Fig. 3(a)). This observation results from the ability of the 3D cellulose microfibers network of the Whatman paper to provide strong capillary forces for the diffusion of CTAC@AuNPs from

colloidal solution. The effect of the optical density of CTAC@AuNPs paper platforms was subsequently evaluated by SERS, by employing p-ATP molecule as active Raman probe, due to its strong affinity for Au surface via thiol linking, its ability to form a self-assembled monolayer as well as its distinct Raman vibrations [10]. After dropping 10 µL ethanolic solution of 10^{-5} M p-ATP onto the dried CTAC@AuNPs papers with different optical densities -obtained after three successive dipping steps- we observe that all paper platforms are Raman active. Moreover, all recorded spectra exhibit similar Raman peak positions, except their intensities which vary as function of the concentration of CTAB@AuNPs loaded onto the paper (Fig. 3(b)). To note that all spectra are dominated by three major Raman bands: i) at 387 cm $^{-1}$ assigned to δ(C-S), ii) at 1075 cm $^{-1}$ assigned to ν(C-S) and iii) 1585 cm $^{-1}$ assigned to ν(C-C).

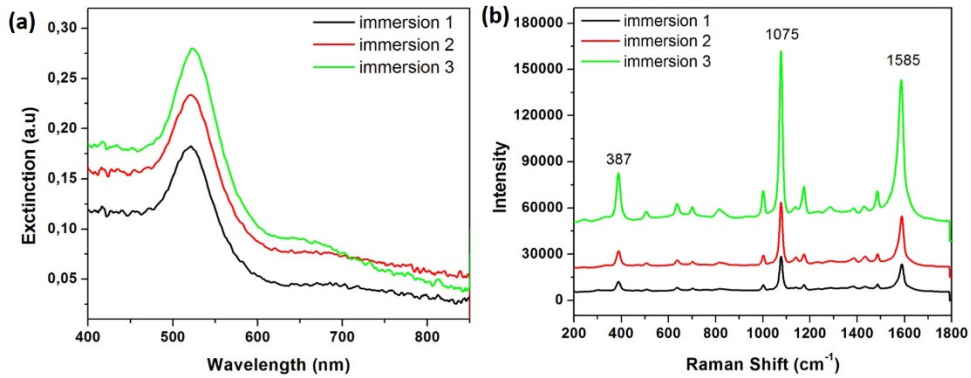

Fig. 3. (a) The optical response of the fabricated CTAC@AuNPs paper nanoplatforms with different nanoparticles concentration, (b) together with their SERS efficiency evaluated using the p-ATP analyte and excitation laser at 785 nm.

As a result, we found that the SERS intensity increases with the concentration of the CTAC@AuNPs loaded onto the paper platforms. However, we assume that the higher SERS efficiency obtained after three immersion steps (green spectrum in Fig. 3 (b)) are also due to plasmon coupling, which generates an enhanced electromagnetic field in the interparticle gaps, operating as effective SERS hot spots for p-ATP detection.

CONCLUSIONS

In conclusion, a simple and efficient plasmonic paper-based nanoplatform with enhanced SERS efficiency was designed. The positively charged CTAC@AuNPs bind electrostatically to the negatively charged cellulose fibers as a result of an easy immersion approach. Notably, the optical properties of the CTAC@AuNPs are well-preserved after the loading, moreover the concentration of the loaded nanoparticles can be increased by several consecutive immersions without harming their optical response. The CTAC@AuNPs paper-based nanoplatforms exhibit SERS performances when the p-ATP Raman reporter is employed. All samples present the vibrational spectrum of the p-ATP molecule, with increasing the optical density the SERS spectra are strongly amplified. Our plasmonic paper-based SERS nanoplatform relies on simple and cheap but highly sensitive and efficient fabrication and detection strategies becoming, therefore, interesting and reliable for analyte detection in complex samples.

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