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Plasmonic Nanoparticles Decorated Salty Paper Based on SERS Platform for Diagnostic low-Level Contamination: Lab on Paper

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Abstract: In this research, a low cost, portable, disposable, environment friendly and an easy to use lab-on-paper platform sensor was made. The sensor was constructed using a mixture of Rhodamine-6G and gold nanoparticles also Sodium chloride salt. Drop–casting method was utilized as a technique to make a platform which is a commercial office paper. A substrate was characterized using Field Emission Scanning Electron Microscope, Fourier transform infrared spectroscopy, UV-visible spectrophotometer and Raman Spectrometer. Rh-6G Raman signal was enhanced based on Surface Enhanced Raman Spectroscopy technique utilized gold nanoparticles. High Enhancement factor of Plasmonic commercial office paper reaches up to 0.9 x10^5 because of local surface plasmonic resonance. While for salty plasmonic commercial office paper, it grows up to 1.11 x 10^5. Particularly the unique properties of commercial office paper like low porosity, flexibility, portable, and high hydrophobicity are well suited for analysis of sample with arbitrary shapes and trace concentration as well as easily transferred to lab. From all the above, it is an excellent candidate for using as a lab-on-paper.

Keywords: Lab-on-Paper, gold nanoparticles, Surface Enhanced Raman Spectroscopy

Introduction

Lab-on-paper is alternative technique to manufacture easy to use, cheap, and portable which demonstrating great promising for forensic science, eco-friendly protection, and food safety mechanism [1-3]. Paper platforms are mostly classified based on their mass which can be shared in three groups: Light paper, standard paper and cardboard. Commercial office paper COP is one of the standard paper whose grammage is in the range 80 – 200 g m^{-2} with thickness 100 µm . Every type of paper was characterized by porosity and hydrophylicity where porous assembly controls colloidal moving. The major attributes of cellulose fiber paper such as the thickness, sample loading ability, low- weight, disposable, elastic (rolled or folded), and annual renewability serve as the versatile SERS substrate[4].

This technology will enabled patterning paper to create millimeter- sized channels that define hydrophilic channels, fluid reservoirs and reaction zones. Furthermore, the emphasis is now on adapting principles of developments in nanotechnology [5], biotechnology [6] to paper-based diagnosis. Surface-enhanced Raman spectroscopy (SERS) identified as a potentially powerful technique could provide a non-destructive and sensitive in molecular detection, combining the specificity of vibrational Raman spectroscopy, with the increased plasmon assisted scattering, induced by metal nanostructures. Noble metal nanoparticles exhibit a localized surface plasmon resonance (LSPR) due to the interaction between incident light and surface electrons present in the metal conduction band.

The LSPR depends on the particle material, size, shape and chemical composition of the metallic NPs and inter-particle spacing [7]. Gold and silver nanoparticles are the most attractive for unique optical and biological properties.

From these, gold nanoparticles (GNPs) are commonly employed to prepare SERS substrates because not only they have higher chemical stability and biocompatibility, but also their surface can be easily modified. This has led to many applications, including diagnostics, therapeutics, optical sensing and photovoltaic[8,9]. Any changes to the environment of these particles (i.e., surface absorption/ desorption of chemical reagents, aggregation, medium refractive index, etc.) will change local electromagnetic field surrounding the GNPs [10]. For instance, the GNPs aggregation (by centrifugation or salt addition) has been used to improve the SERS signal, since the interstitial gaps formed between nanoparticles are hot spots, i.e. zones of particularly give rise to large surface plasmon resonances to yield strong SERS signal enhancement of entrapped Rh-6G contamination.

The aim of this work, is to prepare an efficient a portable sensor (lab-on-paper) for contamination.

Materials and Method

In this work, 20 nm gold quasi-spherical GNPs capped with citrate were purchased from Nitparticles Co., Spain. These GNPs possess exceptional physical and chemical properties. Citrate GNPs are considered as an excellent candidates to be functionalized since a wide range of molecules can be treated onto the GNPs surface using a thiol (SH) group relocating adsorbed citrate anions. Average diameter is 20.1 ± 2.4 nm, Peak SPR wavelength is 522 nm, molar concentration is 1.1 nM, and particle concentration is 6.5×10^{11} particles/mL.

COP presented here is a 135 g m^{-2} *grammage* paper made from the Portuguese paper manufacturer the *Navigator* Company. 20 mM Sodium chloride (NaCl) was purchased from Romil Ltd. Co., United Kingdom, with assay percentage 99.5% and a molecular weight of MW=58.44 Kg/Mol.

Sample Preparation

Raman Substrate Preparation

Raman measurements were done on a COP with an analyte solution (Rh-6G) at concentration of 6 x 10^{-5}. A drop casting technique was used to fabricate the sensor. About 10 µL a micropipette was utilized for all steps. A drop of Rh-6G was applied on a paper substrate and left to dry at the room temperature, then Raman spectra are measured at three random locations as in Fig. 1.

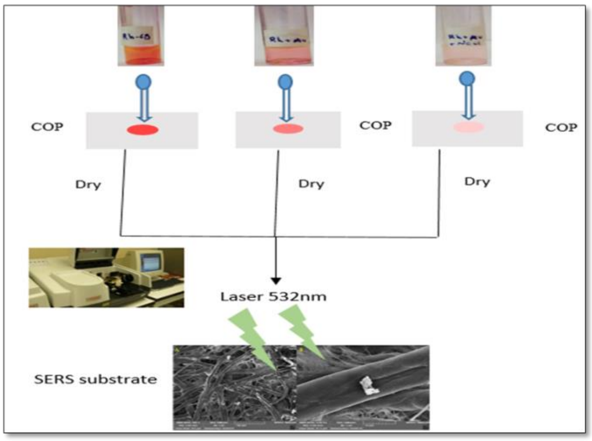

Fig.1: Schematic representation detection by paper-based SERS substrates (aggregated NP-loaded COP)

SERS Substrate Preparation

SERS measurements were performed for COP without and with NaCl. A colloidal 99% of GNPs and 1% of Rh-6G solution was added to make a dilute concentration to construct plasmonic paper.

On the other hand, 89% of GNPs, 1% of Rh-6G and 10% of NaCl colloidal was applied on paper to construct salty plasmonic paper.

Surface Enhanced Raman Scattering (SERS) Measurements

For SERS measurements, few steps are required:

1- A suitable 532 nm diode laser Raman spectrometer with 30 mW power excites Rh-6G –COP strips. Scattered Raman signals were collecting and identifying by intensity measurements at different wavelengths.

2- SERS measurements were taken to plasmonic paper and salty plasmonic paper to estimate the enhancement factor (EF) of the proposed SERS substrates also Raman signal intensity of Rh-6G on a plane COP substrate was measured.

The EF of the proposed substrate is calculated as follows [10]:

$$EF = \frac{I_{SERS}\, C_{Raman}}{I_{Raman}\, C_{SERS}} \quad (1)$$

Where, $\mathbf{I_{SERS}}$ and $\mathbf{I_{Raman}}$ are Raman signal intensities of Rh-6G with plasmonic paper , salty plasmonic paper SERS substrate and Rh-6G reference substrate respectively while $\mathbf{C_{Raman}}$ and $\mathbf{C_{SERS}}$ are the concentration of Rh-6G and Rh-6G - plasmonic , Rh-6G - salty plasmonic respectively .

Results and Discussion

In order to describe and analyze plasmonic and salty plasmonic cellulose-based substrates, Commercial Office Paper COP, morphological and optical properties were done.

Morphological Characterization:

Fourier Transform Infrared Spectroscopy (FTIR)

Overall types of office paper shows the bands related to cellulose fibers, for example OH, C−H, and C−O stretching bands, at 3400 cm^{-1}, 2900 cm^{-1}, and 1060 cm^{-1}, respectively. It is also noticed a peak at 1640 cm^{-1} for the O–H bending vibration which associated with the absorbed H_2O. The (3600–3100) cm^{-1} wide band in the section be responsible for data concerning the hydrogen bonds. The peaks from amorphous cellulose are narrower and have less signal, which can be related with the scission of the intra- and inter-molecular hydrogen bonds. The FTIR spectrum of GNPs emptied on standard paper is presented in Fig.2 .

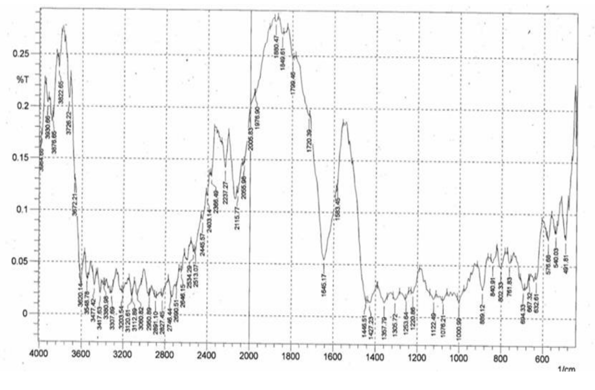

Fig.2: FTIR spectra for GNPs with Rh-6G and NaCl emptied on paper

The peaks looking between 400 cm^{-1} and 600 cm^{-1} are allocated to the metal–oxygen (M–O) stretching mode. The figure displays that the absorption band performed at 3244 cm^{-1} because of NH_2 in the spectra of Rh-6G.

The powerful absorption band seemed at 1635 cm^{-1} in the spectrum has been assigned to C=C. In the spectrum of Rh-6G, this band shown at 1583 cm^{-1} may be assigned to C=O stretching vibration which is agree with [12].

The three peaks, centered at 1000 cm^{-1} , 1357 cm^{-1}, and 1645 cm^{-1} are allocated to the stretching modes of carbonate (CO_3) complexes corresponding to a metal. The existence of these chemical groups on the gold particle surface shows the presence of Au-O compounds where this end result has the same discussion in .The peak observed at 2520 cm^{-1} (attributed to the presence of − SH group), is absent in the spectrum of GNPs because of the foundation of a strong Au-thiol bond. FTIR analysis was done to discover the vibration mode of chemical compounds present on GNPs. The sharp peak of GNPs at 3785 cm^{-1} is probably an O−H stretch, indicating the existence of phenols. The GNPs peaks at 2917 cm^{-1} and 2836 cm^{-1} are indicative of C−H and H−C=O bonds [6].

Field Emission Scanning Electron Microscope (FESEM)

The surface morphology of COP substrates was inspected by Field Emission Scanning Electron Microscope (FESEM). The result displays the cellulosic fibers as in figure (3).

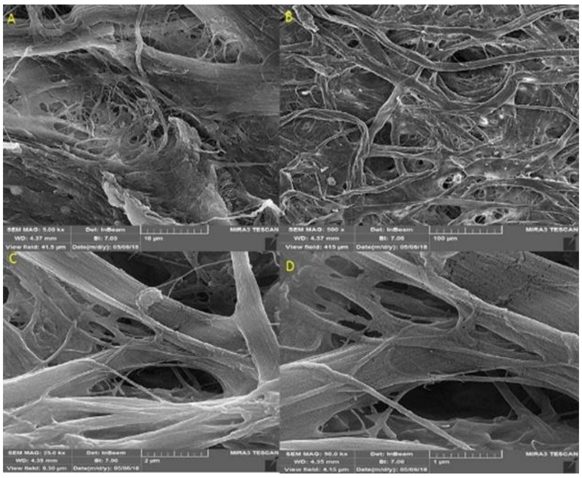

Fig. 3: SEM for office paper with different magnification

The paper has a larger inherent heterogeneous structure abound with many minute opening named pores and fibers of altered sizes. The morphology of cellulose paper shown broad fibers greater than 20 μm established in a medium of small fiber less than 5 μm .The fibers are interlaced within each other in specific COP paper as in figure (3) .COP platform has a more uniform surface, with different profiles and dimensions also it has smaller porosity approximately 49% and greater hydrophobicity where the water-contact angle equals 106° [4]. Accumulated GNPs could be observed at plasmonic paper as in Fig.4 where, the dense layer of GNPs is probably resulting from colloidal GNPs accumulation upon drying making the irregular clusters of GNPs onto the paper substrate. These accumulation of GNPs can support a good adsorption ability by capillarity force .

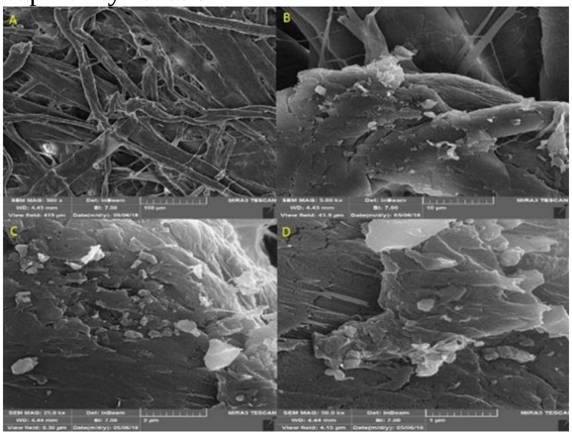

Fig. 4: SEM for GNPs with analyte Rh-6G on COP paper

The office paper revealed a high homogeneity of GNPs distribution without the formation of visible aggregates. More GNPs were fill in inside bulk and form adsorbed coating on the surface according to matrix , low porosity and high hydrophobicity, also the adsorbing of nanoparticles on paper surface due to van der Waals boundaries. The distribution and adsorption of GNPs on paper appears to be mostly well-ordered by the three dimensional fibers system of paper that supply altered powerful capillary action for the diffusion of GNPs from colloidal . FESEM was scanned the morphology of the salt plasmonic paper surface. Figure 5 clearly established the spreading of great-density GNPs on the porous bare of cellulose fibers due to the NaCl -made accumulation. Therefore, the aggregation possibly resulting from electrostatic screening of the negative charges around the GNPs by the salt ions to form clusters of GNPs by interacts each particle with the neighboring one on the fiber substrate with more irregular structures and tips. Then the volume of the enhanced field is comparative to the dimensions formed by particles surrounding a single GNP. The assembly of GNPs clusters has nanosized gaps between two or more neighboring structures, i.e. hot spots are in nanoscale.

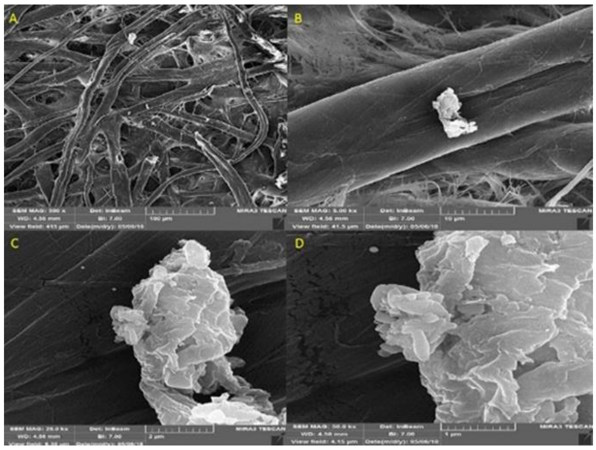

Fig. 5: SEM of GNPs after introducing NaCl

Optical Characterization Results

The optical properties of plasmonic and salty cellulous platform paper are very significant, particularly when cellulose platform used for sensing field. It is important to recognize how variations in the structure of cellulose paper will affect the optical properties.

UV-VIS Absorption Spectroscopy Results

The absorption spectra of pure GNPs, alone Rh-6G dye on COP, mixture of Rh-6G – GNPs-COP, plasmonic paper, and finally mixture of Rh-6G - GNPs -NaCl salt-COP, salty plasmonic paper, are presented in Fig.6 .In the case of pure GNPs (figure 6 a) displayed a single but strong surface plasmon resonance SPR position was located at band 522 nm usually indicates that GNPs will be less than 60 nm. Figure (6b) shows the maximum absorption of Rh-6G paper was at ~530nm wavelength. The optical properties of gold nanoparticles change when particles aggregate and the conduction electrons near each particle surface become delocalized and are shared amongst neighboring particles. So, it is obvious that the plasmonic paper shifted the surface plasmon resonance to lower energies .i.e. the wide and lower absorption spectrum possibly because of the accumulation of GNPs on the COP cellulose fiber. Notably, the positioning of the second small SPR peak appears in ~780 nm (figure 6c), due to increasing particle size i.e. the structure of the sphere particles will be irregular. The first peak refers to sphere GNPs while the second one refers to irregular shape. Furthermore, salty plasmonic paper increased local field associated with hotspots due to aggregated of nanoparticles. As in figure (6d), more broadening, shifting to long wavelengths, decreasing the intensity of absorption, second peak at 890 nm were noticed in spectrum . That attributed to the chemical interface damping between NPs in salt solution and decreasing the surface area to volume ratio of part of nanosphere which comes from adsorbed it by salt. Surfactant Citrate capping on the gold nanoparticle forms a layer of electrostatic repulsion, which prevents the aggregation of the nanoparticles. The role of Electrolytes, solution of NaCl, screens the repulsive electrostatic forces of the citrate layer and induces aggregation.

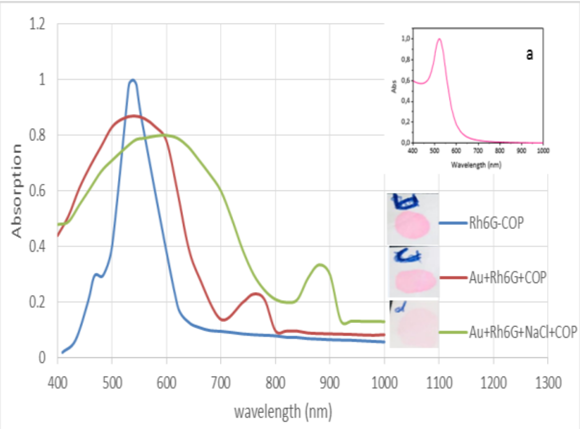

Fig. 6 Absorption spectrum of (a)GNPS (b)Rh-6G+COP (c) Rh6G + GNP+COP(d) Rh6G + GNPs+ NaCl+COP.

(SERS) of commercial office paper (COP)

SERS is a powerful technique to the discriminate, identification, and potential quantification of certain COP composition when fabrication lab on paper sensor starts by defining grooves and reaction areas onto COP paper using Raman spectroscopy. At first, Raman spectrum was obtained on plane for COP, the peak observed at ~1094 cm^{-1} where it is ascribed to the C−O−C bending mode of cellulose fibers. COP cellulose platform appears low scattering due to low porous structure and the random cellulose matrix. The structure of COP was changed when taken some promising steps to be appeared more enhancement therefore, Raman spectra of Rh-6G paper, plasmonic paper and salty plasmonic paper, all of them on COP were depicted in figure (7).

In Figure (7) a, Raman spectrum of Rh-6G is presented which Rh-6G is a common probe for this analytical technique. After adding Rh-6G solution, the effort of Rh-6G liquid was dominated by diffusion due to cellulose channels of COP , the solution was dried completely at 45 minutes with homogenous dark pink stain without any "coffee-ring" effect, i.e. Rh-6G molecules adsorption are well-ordered, because of low pores and poor heat transfer fluids .

Generally, the signals are inherently low, so a minimal number of scattered photons are available for detection because of faint concentration. Furthermore , in this experiment Rh-6G absorption spectrum molecule is resonant with laser wavelength which is enhanced Raman signal.

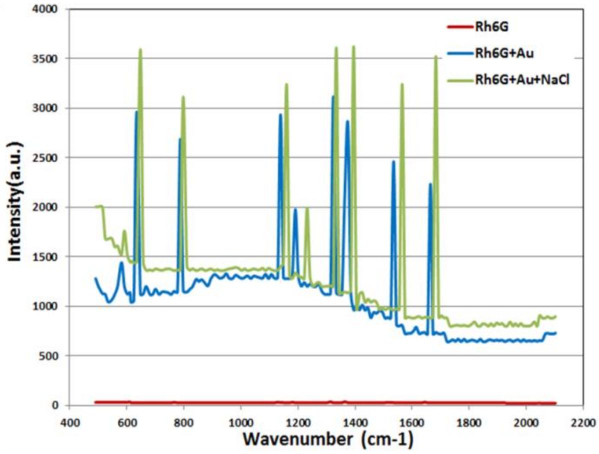

Fig. 7 : SERS spectra of Rh-6G paper, plasmonic paper , salty plasmonic paper

Figure,(7)b- displays SERS spectrum of plasmonic COP , the colloid prevails into the paper and dries almost instantly at 28 minutes due to high thermal diffusivity of nanofluid relative to alone Rh-6G where the GNPs has high thermal conductivity . This phenomenon could be due to the electrostatic interaction between the cationic Rh-6G and the negatively charged GNPs beside a Sulfur groups on the surface of GNPs authorized the binding and diagnosing then, enabling a light pink semi - uniform distribution spot on COP surface. In case of alone Rh-6G , its spectral intensity is very low, so in order to enhanced the signal a very small quantity of GNPs was applied due to SPR mechanism ,then, the intensity is almost giant and the peaks become more distinguished.

SERS effects action occurred usually on two reasons: (1) long –range resonant surface plasmon excitation of GNPs-Rh-6G where the electromagnetic field was enhanced due to localized surface plasmon resonance (LSPR) in the near-field GNPs surface, and hot spots of the GNPs liquid cluster. (2) short- range chemical impact, the chemical boosting is because of the charge transfer (CT) mechanism between the GNPs and Rh-6G due to the neighborhood .If the surface of the GNPs was not capable of adsorbing Rh-6G, then SERS effects would be hard to prompt. Efficiently, the enhancement factor EF was 0.9×10^{5}.

Perfectly, SERS platform should not only have many numbers of hotspots and ability of low-diagnosis limit but also should be multilateral in different parts such as reproducibility, regularity, scalability, and economical factor. Herein, typical route have been pursued to improve the efficacy of paper-based SERS platforms by salt-induced accumulation of GNPs. Salty plasmonic paper was a good choice to enhanced the signal by adding NaCl salt to plasmonic colloidal and applied it at COP when SERS was achieved as in figure (7)c with enhancement factor $1.11x10^{5}$. The aqueous solution was dried after 21 minutes with a small diameter faint color stain than others because of the accumulation. The accumulation of the GNPs was influenced by environmental parameters (pH and ionic strength) also external factors such as light and heat.

The three dimensional network of cellulose fibers on paper enables the transition of GNPs in colloidal solution to solid state with accumulation of GNPs also promote the adsorption of the Rh-6G analyte to GNPs or it may make re-orientation or Rh-6G at the GNPs surface. Multiple GNPs in cluster with sharp edges, and areas of large curvature of GNPs on the order of 10–100 nm when brought together to form accumulation yielding high field strength and many orders of magnitude greater than the fields at the surface of individual GNPs. This could be attributed to the coupling of their transition dipoles, that is, each particle's enhanced field interferes coherently at the junction between the accumulated GNPs.

SERS signal will be affected based on three reasons: (a) an increase in the EM field at the junction between the particles, (b) CT also possibly contributes to the enhancement, and (c) absorption/ reorientation of the analyte is likely because of the induced anion.

To test the reproducibility of all above optimized SERS substrate , more than 5 spectra were obtained at randomly selected sites on the commercial office paper substrate . Also the same procedure will be taken for six weeks sequentially where the results appear approximately the same behavior with 5% difference range. In certain cases, a small peak shift was noticed and exhibited selective enhancement, and this could be because of the orientation of molecules on the paper substrates.

Conclusion

The essential encounter for the SERS is to develop a cheap, easy to handle, pliable, and sensitive workable SERS platform by synthesized active plasmonic SERS substrate with low porosity and high hydrophobicity which is an impact factor in the homogeneity of the SERS signal acquired with COP cellulous fiber .An ideal portable miniature platform for the detection of adsorbed Rh-6G molecules with high specificity and sensitivity, especially for tracing concentration like explosive detection in countering terrorist extortions, trace amounts of contaminants, pollution of soil was built.

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الليزر المعزز للانحلال التحفيزي للمثيلين الأزرق المبني على أساس انتقال الشحنات السطحية باستخدام المحفز أوكسيد الزنك النانوي الملدن

أمين وليد جبار   زينب فاضل مهدي   رواء احمد فارس   هبة كاظم وهاب

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الخلاصه: الورق الملحي المزخرف بالجسيمات النانوية المبني على تعزيز اطياف رامان بالكشف عن الملوثات ذات المستوى الواطئ :مختبر على ورقة الخلاصه في هذا البحث تم تصنيع قاعدة متحسس كمختبر على ورقة ، رخيص، سهل الحمل ،قابل للاستخدام مره واحدة ،صديق للبيئة وسهل الاستخدام . تم بناء هذا المتحسس باستخدام خليط صبغة الرودامين (الملوثة) مع جسيمات الذهب النانوية بالإضافة الى ملح كلوريد الصوديوم. استخدمت طريقة القطرة كتقنية لصنع متحسس محمول على ورق المكتب التجاري . تم فحص العينات بأستخدام مجهر الالكترون الماسح ذات المجال المنبعث و مطياف فورير المتحول للاشعة تحت الحمراء ومطياف الاشعة فوق البنفسجية – المرئية ومطياف رامان . تحسن اشارة رامان للرودامين بالاعتماد على تقنية تعزيز مطياف رامان بالاستفادة من جسيمات الذهب النانوية. الزيادة العالية في معامل البلازمونك لورق المكتب التجاري وصل الى 0.9×10^5 وذلك بسبب الرنين البلازموني السطحي. بينما معامل الورق المكتب التجاري الملحي البلازموني قد زاد الى 1.11×10^5 بصورة خاصة، الصفات الفريدة لورق المكتب التجاري مثل المسامية المنخفضة ،المرونة وغير محبة للماء كثيراً مناسبة لتحليل العينات الملوثة الغير منتظمة الشكل وذات تراكيز واطئة جداً حيث يمكن نقلها بسهولة الى المختبر . من جميع ما جاء اعلاه ،العينة المنتجة من ورق المكتب التجاري يمكن ترشيحها كمتحسس كفوء كمختبر على ورقة