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ARTICLE

Rapid Fabrication of Self-assembled Interfacial Film Decorated Filter Paper as Excellent Surface-Enhanced Raman Scattering Substrates

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An excellent paper-based SERS substrate was easily fabricated by utilizing an interfacial films formed in the mixture of Ag colloid and CH₂Cl₂. This interfacial film coating method significantly improves the fabrication efficiency of SERS substrates. The substrate has a high coverage of silver nanoparticles (Ag NPs) and can be tailored to arbitrary shapes. The SERS substrate exhibits high sensitivity ($EF \sim 4 \times 10^7$) and gives uniform SERS signals with a relative standard deviation (RSD) of 8.08% (spot-to-spot) and 8.65% (batch-to-batch) using 4-mercaptobenzoic acid (4-MBA) as Raman probe. In addition, this SERS substrate with excellent stability can be stored for more than 30 days. The limit of detection was found to be 10^{-8} M for 4-MBA. In general, this SERS substrate is qualified for rapid and simple trace detection of various analytes.

Introduction

Surface enhanced Raman spectroscopy, with the superiority of high sensitivity, narrow spectral bandwidth and weak water interference, is widely used in various fields such as food safety, materials characterization and drug monitoring.^{1,2} The development of SERS substrates with good reproducibility and stability, high sensitivity and easiness for fabrication has important significance for practical applications of SERS.^{3,4} Nanoparticles self-assembly technique is an important nanotechnology and has been widely explored owing to its simplicity.^{5,6} Uniform and ordered nanofilms can be formed via this approach since the inherent mobility of the liquid/liquid interface can make up for the deficiencies of nanofilms.^{7,8} Moreover, the phase separation behavior can disperse the complexity of the nanoparticle structure.^{9,10}

Recently, numerous studies have demonstrated the advantages of using liquid/liquid interface-mediated self-assembly technique^{11,12} to fabricate SERS substrates.^{13,14} The liquid/liquid interface film was mostly used in liquid phase conditions which has greater flexibility.¹⁵⁻¹⁷ However, the

stability of the self-assembled nanoparticles on the interface is relatively poor and the detection efficiency or the utilization of the substrates is low.¹⁸⁻²⁰ Therefore, some researchers have deposited self-assembled Ag NPs on some rigid substrates such as glass slides, silicon wafer and templated block-copolymer substrates,²¹ which is more convenient to detect analytes and improves the stability of the substrates. But quartz slides need complex pretreatment to ensure the hydrophobicity, which reduces the efficiency of the preparation extremely. Moreover, with the rigid characteristics of the slides, the substrates cannot be cut into arbitrary shapes, so the substrate is not well utilized meanwhile avoiding the cross-contamination of samples.²²

Filter papers, with advantages of low cost, with porous structures and good hydrophilia, are widely used in analytical chemistry filed.²³ To fabricate large scale, uniform paper-based SERS substrates, many methods have been developed such as physical vapor deposition,²⁴ laser-induced deposition,²⁵ screen printing,²⁶ ink-jet printing,²⁷ filtering,²⁸ dip coating²⁹ and silver mirror reaction.³⁰ Among them, some methods need large-scale instrumentations; some methods cannot ensure the uniformity

of nanoparticles on the filter paper; some methods are too susceptible to the external environment or consume too much time. In short, almost all methods are not the best choice for practical applications.³¹

In this work, a simple two-step method based on liquid/liquid interface self-assembly technique was developed to fabricate paper-based SERS substrate, which greatly improves the fabrication efficiency (<10 min) and the utilization of SERS substrate. The effect of the number layers of deposited Ag NPs on SERS response of SERS substrate was investigated. The sensitivity, uniformity and long-term stability of the substrate were evaluated using 4-MBA as Raman probe and both parameters are excellent.

Experimental

Materials

Silver nitrate (AgNO_3), sodium citrate, tetrabutyl ammonium nitrate ($\text{TBA}^+\text{NO}_3^-$), 28% ammonia and 30% hydrogen peroxide were obtained from Xilong Chemical Co., Ltd. (Beijing, China), dichloromethane (CH_2Cl_2) was obtained from Tianjin Bodi Chemical Co., Ltd. (Tianjin, China), acetone was obtained from Tianjin Fucheng Chemical Reagent Factory (Tianjing, China), 4-Mercaptobenzoic acid (4-MBA) was obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), qualitative filter papers (Medium) were obtained from Fushun Civil administration Filter Paper Factory (Fushun, China), quartz slides were obtained from Nantong Ruisen Optical Technology Co., Ltd. (Nantong, China), deionized water was used for all procedures. All chemicals were used as received.

Preparation of silver colloid

Silver colloid was prepared according to the Lee and Meise method.³² Briefly, 45 mg of silver nitrate was added to 250 mL of deionized water, which was then brought to a boil in a flask under vigorous stirring. 5 mL 1% Sodium citrate, was added, and the solution was kept boiling for 1 hour. Finally, the silver colloid was cooled naturally after the solution turned to greenish brown.

Fabrication of paper-based SERS substrate

The fabrication process of liquid/liquid interface self-assembled Ag NPs decorated filter paper SERS substrate is shown in Figure 1. Firstly, 4 mL aqueous Ag colloid and 2 mL CH_2Cl_2 were added into a 10 mL centrifuge tube³³ (mainly consisted of polytetrafluoroethylene (PTFE) which is water repellent) and the mixture was vigorously shaken for 2 min. Let sit for 5 minutes, a film of Ag NPs was formed on the interface of silver colloid and CH_2Cl_2 . Secondly, appropriate amount of “inducer” $\text{TBA}^+\text{NO}_3^-$ ³⁴⁻³⁶ was added dropwise until a bright silver mirror film formed on the water/oil interface. Because of the affinity between CH_2Cl_2 and centrifuge tube wall, the formed silver mirror film surrounds the water phase. Therefore, part of the silver mirror film was exposure to air as water phase is on the upper part and adjoin air. In order to perform the coating

process more convenient, some of water and CH_2Cl_2 were removed. Then, filter paper was lightly dipped on the silver mirror film to deposit self-assembled Ag NPs on filter paper. The tube was tilted to provide a large surface of silver mirror film. Finally, the fresh prepared substrate was dried in oven and shielded from ambient light.

To fabricate paper-based SERS substrates decorated with multilayer self-assembled Ag NPs, additional layer Ag NPs were deposited by repeating the method used to prepare monolayer substrates. And the former layer Ag NPs should be completely dried before the next layer deposited on it.

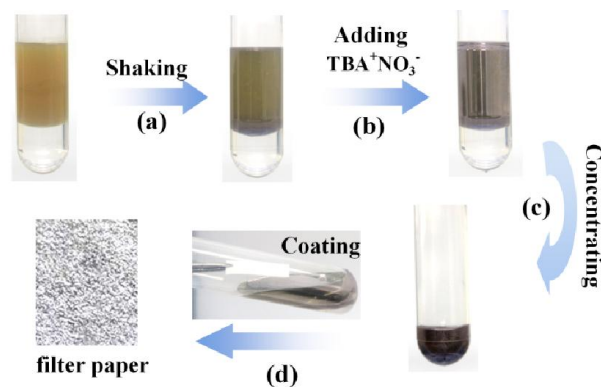


Fig. 1 Preparation procedure of liquid-liquid interface self-assembled Ag NPs decorated filter paper.

Ag NPs deposited on quartz slides was prepared using the same method. Particularly, the quartz slides need pretreatment to ensure the hydrophobicity of the slides. Concrete processes are as follow:²² quartz slide was firstly immersed in acetone and sonicated for 20 min, then it was treated with the mixture of 28% aqueous ammonia and 30% hydrogen peroxide (1/1 V/V) at a constant temperature of 100 °C and removed out. Finally, quartz slide was washed repeatedly with ultrapure water 5~10 times and dried in oven.

To prepare the sample standard solution, 0.0154 g 4-MBA powder was weighed and then dissolved it into 100 mL ethanol. Ethanol solutions of 4-MBA with concentrations of 5×10^{-6} M, 10^{-6} M, 5×10^{-7} M, 10^{-7} M, 5×10^{-8} M, 10^{-8} M were prepared by diluting 4-MBA standard solution with different proportions.

SERS measurement

Raman spectra were recorded using a portable compact laser Raman Spectrometer (BWS415-785H B&W Tek, Inc.). The excitation wavelength of the laser is 785 nm. The spot size of focus laser beam is 10 μm in diameter. The typical laser power and accumulation time was 150 mW and 5 s respectively unless otherwise stated. The distance between laser probe and sample stage is 5.9 mm. The spectrum range of the spectrometer is 175 to 2700 cm^{-1} with a spectral resolution of better than 3 cm^{-1} . Boxcar averaging was used to smooth the raw spectrum, and a baseline correction routine was performed to obtain the final spectrum with the background subtracted.

Results and discussion

In order to evaluate the plasmonic property of the paper-based substrates, the UV-Visible absorption spectra of silver colloid and paper-based substrate were measured. As shown in Fig 2, silver colloid exhibits an appreciable absorption peak at 446 nm, which can be assigned to the plasmon mode of single isolated silver nanoparticles. The paper-based substrate shows an appreciable peak at 386 nm with a weak broad shoulder and a strong broad peak at around 670 nm. The red-shift may be assigned to the transverse plasmon mode of coupling nanoparticles. And the blue-shift region can be assigned to the longitudinal plasmon mode of coupling between multiple nanoparticles.²¹ The blue-shift makes the paper-based substrate to take better use of the 785 nm laser excitation.

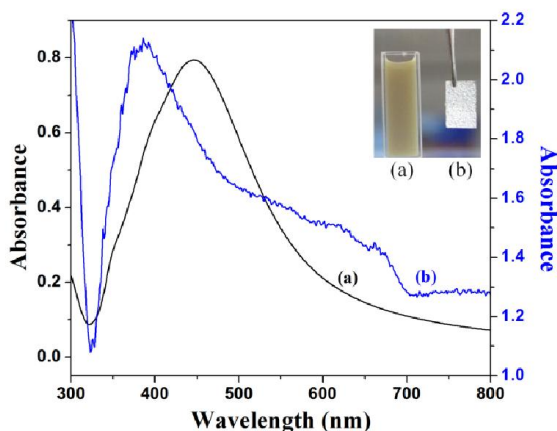


Fig. 2 The ultraviolet absorption spectra of the colloidal solution of Ag NPs (a) and the paper-based substrates (b). Inset: the photos of colloidal solution (a) and the paper-based substrates (b).

Comparison of SERS enhancement of interfacial self-assembled Ag NPs adsorbed on different substrates

To compare the characteristics of self-assembled Ag NPs decorated on different substrates, Ag NPs deposited on quartz slides was also prepared using the same method. 4-MBA was employed as probe molecule for SERS measurement, based on literatures, the strongest Raman peaks of 4-MBA are 1076 and 1586 cm^{-1} , both corresponding to the $\nu(\text{C-C})$ stretch mode.³⁷

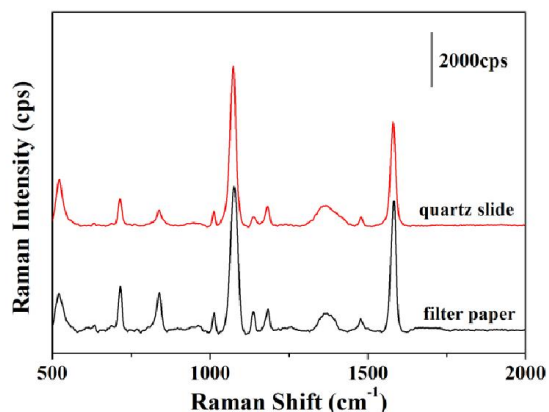


Fig. 2 SERS spectra of the solution of 10^{-5} M 4-MBA, using liquid/liquid interface self-assembled Ag NPs adsorbed filter paper and quartz slides respectively, each spectrum represents the average value from five SERS spectra.

SERS substrates were placed on the slide on objective table. Then, 15 μL of 10^{-5} M 4-MBA ethanol solution were dropped on the paper-based and quartz slide SERS substrate using pipette. Finally, the corresponding Raman spectra were collected. As shown in Figure 2, using filter paper-based SERS substrate can obtain a comparable Raman intensity than quartz slide SERS substrate. Because no pretreatment is needed, it is more efficient to use paper as scaffold material. And this paper-based SERS substrate can be cut into arbitrary shape, which greatly improves the utilization of the SERS substrate. Meanwhile, without waiting for the droplets drying owing to the water conductivity of filter paper, the SERS detection is more convenient and rapid.

Comparison of interfacial self-assembled Ag NPs decorated filter papers with different layers

The scanning electron micrograph (SEM) of prepared silver nanoparticles is shown in Figure 3. The average size of Ag NPs is 50 ± 4 nm analyzed by Image J software.

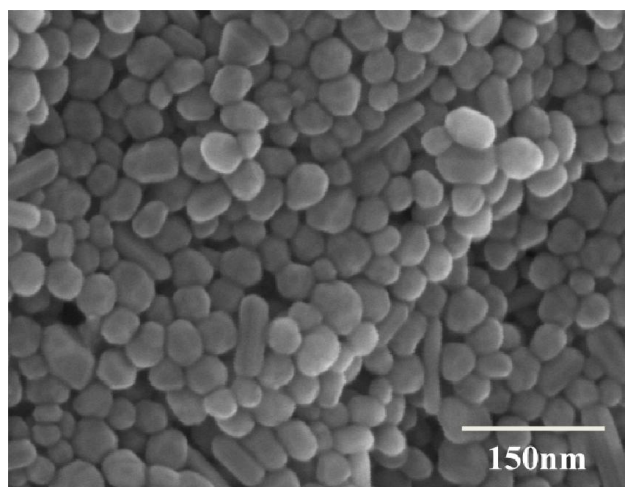


Fig. 3 SEM image of silver nanoparticles, the magnification is 130K.

Previous report has shown that the SERS performance of substrates decorated with metallic nanoparticles strongly depends on the deposition amount of nanoparticles.³⁸ In order to optimize the SERS activity of the SERS substrate, self-assembled Ag NPs were deposited on filter paper with different layers. The SEM images of the SERS substrates deposited with 1~4 layers of Ag NPs are presented in Figure 4. Figure 4(1) illustrates that the monolayer Ag NPs deposited on the paper SERS substrates distribute uniformly, the coverage rate of Ag NPs on the filter paper is about 70%, which is much higher than paper-based SERS substrates prepared by other methods,^{39,40} and almost no Ag NPs clusters with each other. When multilayer Ag NPs are adsorbed on the filter paper, the coverage rate of Ag NPs is almost 100%.

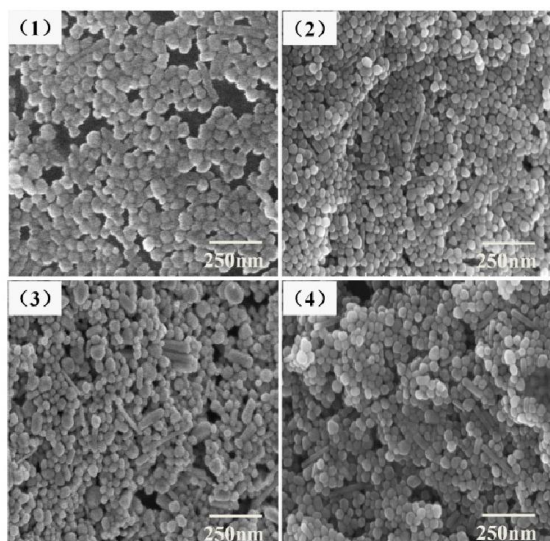


Fig. 4 SEM images of the 1-4 layers liquid/liquid interface self-assembled Ag NPs decorated filter paper SERS substrates, the magnification is 30K.

15 μL of 10^{-5} M 4-MBA ethanol solution were dropped on the paper-based SERS substrates decorated with different layers of Ag NPs. Figure 5 shows the corresponding Raman spectra, indicating that the measured Raman intensity for samples of monolayer Ag NPs substrate is the highest. The SERS intensity decreases as the layer of self-assembled Ag NPs increases. This can be attributed to the different coverage of Ag NPs on filter paper. A relatively low coverage rate will provide more chance to trip 4-MBA molecular into the junction of Ag NPs, which brings a more intense SERS response. On the other hand, when multilayer Ag NPs are decorated on filter paper, Ag NPs have already formed dense clusters, hindering the movement of the filter paper and the generation of real-time hot spots,⁴¹ which is not conducive for sample molecules trapped into the hot spots, so the SERS response of the substrates decreases.

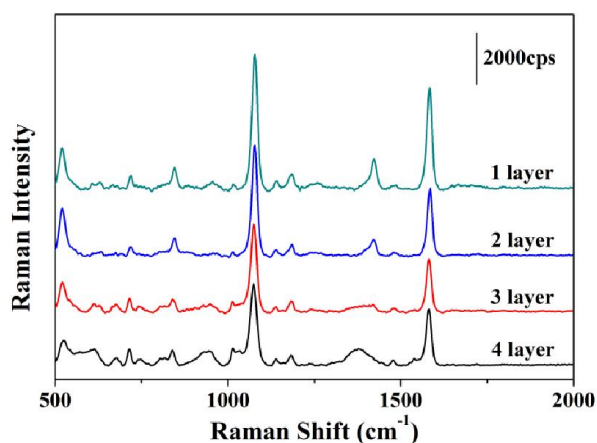


Fig. 5 SERS spectra of the solution of 10^{-5} M 4-MBA using 1-4 layers liquid/liquid interface self-assembled Ag NPs films adsorbed on the filter paper respectively, each spectrum represents the average value from five SERS spectra.

Uniformity of paper-based SERS substrates

To study the spot-to-spot uniformity of the paper-based SERS substrate, the SERS substrate ($1 \times 1 \text{ cm}^2$) was immersed into 10^{-3} M 4-MBA ethanol solution for 2 h followed by rinse thoroughly which could remove 4-MBA molecules attached on filter paper. However, 4-MBA molecules adsorbed on Ag NPs cannot be swept away because 4-MBA has strong affinity to Ag NPs. Thus, the distribution of the Ag NPs on filter paper can be reflected by SERS response of different spots on SERS substrate. SERS spectra of 30 arbitrary spots on SERS substrates were collected (Figure 6). The signal intensities from different spots remained relatively constant. The SERS substrate exhibits a very uniform Raman response, with relative standard deviations (RSD) of 8.88% at 1076 cm^{-1} and 8.08% at 1586 cm^{-1} .

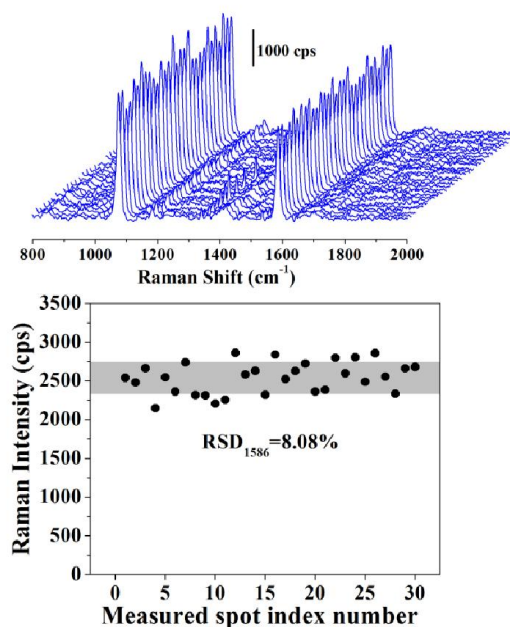


Fig. 6 SERS spectra of 30 arbitrary spots of the SERS substrates ($1 \times 1 \text{ cm}^2$) for 4-MBA (10^{-3} M), the laser pump is 30mW and the integration time is 3 s. The spot size is $10 \mu\text{m}$ in diameter.

To study the batch-to-batch uniformity of the paper-based SERS substrates, 20 SERS substrates were fabricated. Each batch of paper-based SERS substrate was immersed into 10^{-3} M 4-MBA ethanol solution for 2 h followed by rinse thoroughly and each SERS spectra from five spots was collected at the wet condition of the filter paper. The average SERS spectra of each batch were shown in Figure 7. The SERS spectra of 20 batches present little difference of Raman response with RSDs of 10.3% at 1076 cm^{-1} and 8.65% at 1586 cm^{-1} , indicating the SERS substrate has an excellent batch-to-batch reproducibility. These results reveal that the spot-to-spot uniformity and batch-to-batch reproducibility of paper-based SERS substrates are outstanding, which is sufficient to provide reproducible SERS measurement and has broad prospects for quantitative detection applications.

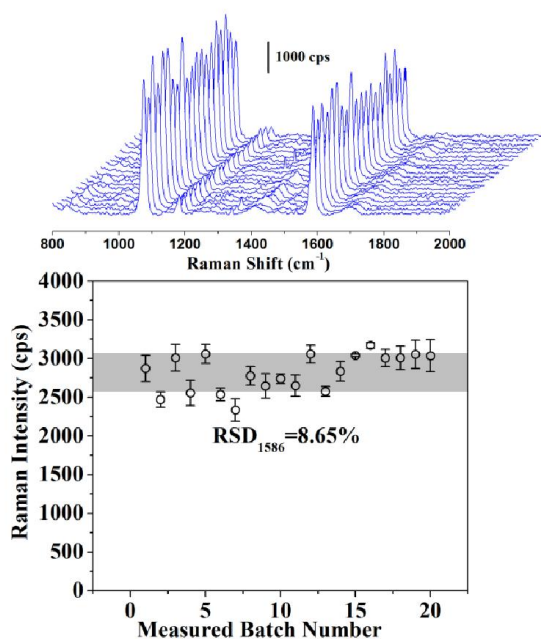


Fig. 7 SERS spectra of 20 batches of the SERS substrates for 4-MBA (10^{-3} M), the laser pump is 30 mW and the integration time is 3 s. The spot size is $10\ \mu\text{m}$ in diameter. Inset: SERS intensity distribution of the $1586\ \text{cm}^{-1}$ band. Each data point represents the average value from five SERS spectra. Error bars show the relative standard deviations.

Time stability of paper-based SERS substrates

Long term stability of SERS substrate plays a crucial role for the practical applications. However, silver nanostructures have disadvantage of instability all the time. Figure 8 describes the time dependence of Raman signal of the paper-based SERS substrates. SERS spectra were collected every 3 days within a month. As a result, there was no apparent change in the intensity of SERS signal even after the SERS substrates were fabricated for 30 days. This paper-based SERS substrate demonstrates pretty long-term stability, making it a promising sensing device for real-world sensing applications.

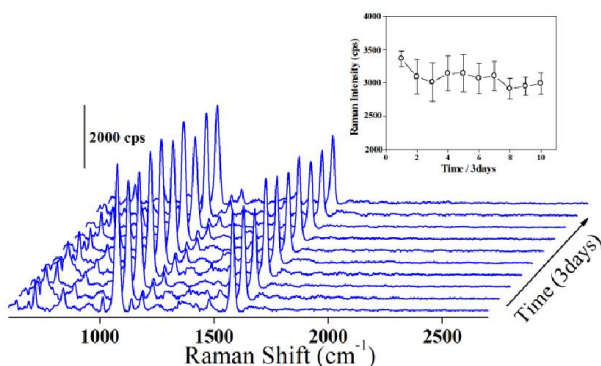


Fig. 8 SERS spectra of 10^{-5} M 4-MBA dropped onto filter paper substrates every three days within a month. Inset: SERS intensity distribution of the $1586\ \text{cm}^{-1}$ band. Each data point represents the average value from five SERS spectra. Error bars show the relative standard deviations.

Enhancement factor (EF) and sensitivity of paper-based SERS substrates

Firstly the paper-based substrate was immersed in 1mM 4-MBA ethanol solution for 30 minutes, and then washed thorough to remove 4-MBA molecules which were not adsorbed on the surface of Ag NPs and the filter paper. Then the monolayer 4-MBA molecule could be adsorbed on the surface of the substrate and the SERS spectrum was measured at the wet condition of the filter paper.

Enhancement factor was defined as the following equation:⁴²⁻⁴⁴

$$EF = \frac{I_{\text{SERS}}}{I_{\text{bulk}}} \times \frac{M_{\text{bulk}}}{M_{\text{ads}}}$$

where I_{SERS} and I_{bulk} are the integrated intensity of the characteristic Raman peaks of 4-MBA molecules on the filter paper substrate surface ($1076\ \text{cm}^{-1}$, $1586\ \text{cm}^{-1}$) and on the powder ($1096\ \text{cm}^{-1}$, $1593\ \text{cm}^{-1}$), respectively (Figure 9). The intensity at $1076\ \text{cm}^{-1}$ and $1586\ \text{cm}^{-1}$ were both used to calculate EF values. M_{bulk} is the molecule number of the neat 4-MBA in the laser illumination volume, which can be determined by the laser spot ($10\ \mu\text{m}$ in diameter) and the penetration depth ($12\ \mu\text{m}$) of the focused beam. M_{ads} is the number of molecules adsorbed and sampled on the filter paper substrate within the laser spot, which is determined by the following equation:⁴⁵

$$M_{\text{ads}} = N_{\text{d}}A_{\text{laser}}A_{\text{N}}\rho_{\text{b}}$$

where N_{d} is the number density of NPs, A_{laser} is the area of the laser focal spot, A_{N} is the NP's footprint area, and ρ_{b} is the bonding density of 4-MBA molecule.³⁷ N_{d} and A_{N} can be obtained from the SEM images and analyzed by Image J software. $N_{\text{d}}A_{\text{N}}$ was $\sim 66.8\%$ after calculation; the EFs were calculated to be 2.9×10^7 and 4×10^7 , respectively.

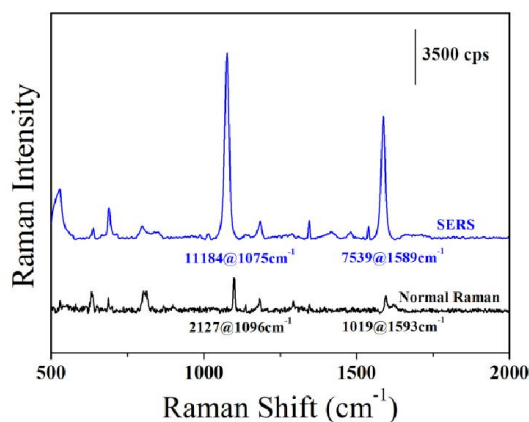


Fig. 9 Normal Raman spectrum of 4-MBA solid powder and the SERS spectrum of 1 mM 4-MBA ethanol solution, each spectrum represents the average value from five SERS spectra. The laser pump is 30 mW and the integration time is 5 s.

SERS spectra of 4-MBA ethanol solution with different concentrations of 10^{-5} M– 10^{-8} M on SERS substrates were

recorded (Figure 10). SERS intensity corresponding to around 10 times of the noise level could be obtained at the concentration of 10^{-8} M 4-MBA. Therefore, the limit of detection of 4-MBA was found to be 10^{-8} M. The interfacial self-assembled Ag NPs decorated filter paper SERS substrates present high sensitivity and have significances for detection of trace pollutants.

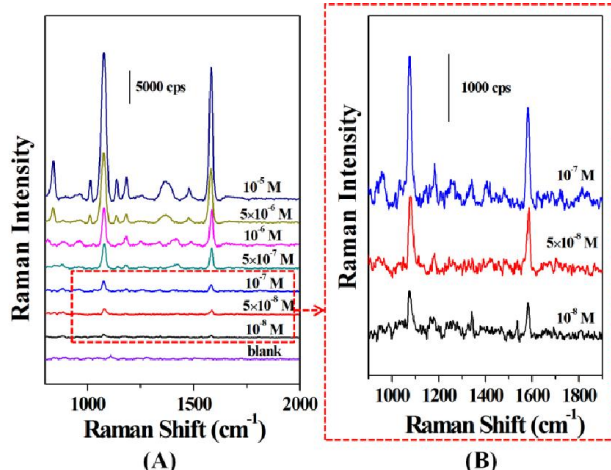


Fig. 10 (A) SERS spectra of the 4-MBA with different concentrations, each spectrum represents the average value from five SERS spectra. (B) Magnified views of the SERS spectra for the low-concentration regions. The laser pump is 150 mW and the integration time is 10 s.

To study the relationship between SERS intensity and the concentration of analyte, 4-MBA of each concentration was selected as model analyte. Figure 11 shows a function of concentration and Raman intensity for 4-MBA over the range of 10^{-5} – 10^{-8} M. At all vibrational bands, the SERS intensity mapped onto the variation in sample concentration, which indicated that quantitative analysis of analyte could be performed on this paper-based SERS substrate.

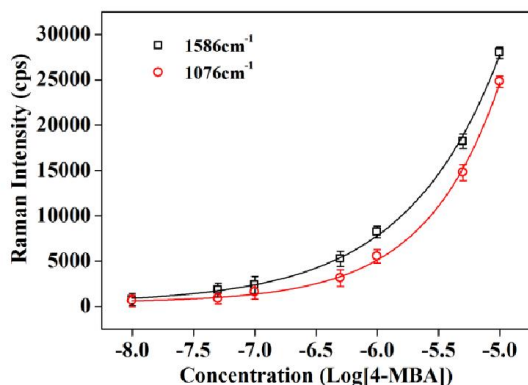


Fig. 11 The concentration dependence of the Raman intensity at two bands for 4-MBA. Each data point represents the average value from five SERS spectra. Error bars show the relative standard deviations.

Conclusions

In summary, self-assembled Ag NPs decorated filter paper was easily fabricated as excellent SERS substrates using interfacial film coating method. This method dramatically improves the efficiency of fabrication and the coverage of Ag NPs on paper. Different layers of Ag NPs decorated filter paper SERS substrates were compared and the Raman response of monolayer adsorbed substrates is the highest. The uniformity and the reproducibility of the paper-based SERS substrates are both splendid which is critical for the quantitative determination. The stability of this substrate can ensure their quality for more than 30 days after initial preparation. The LOD can reach to 10^{-8} M for 4-MBA, which implies high sensitivity of the SERS substrates. At the same time, through the approach in this work, the preparation process is rapid and cost-effective. With these advantages, this method allows large scale fabrication of highly sensitive SERS substrate and has great potential for food safety, environment monitoring, and detection of other hazardous matter.

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