SERS-ACTIVE NON-PLASMONIC SUBSTRATES BASED ON CONDUCTING POLYMERS

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Abstract

Surface-enhanced Raman scattering (SERS) spectroscopy is a highly sensitive, important non-contact analytical technique valued for its sensitivity and ability to provide unique molecular fingerprints. Although traditional SERS platforms rely on plasmonic metal nanostructures, there is a growing interest in developing alternative, non-plasmonic SERS-active materials. Among them, conducting polymers, such as quaterthiophenes or thiophenes, are highly promising candidates due to their cost-effectiveness, flexibility, and ease of processing. This study explores the SERS performance of spin-coated and thermally cured poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) films and demonstrates that the SERS activity of PEDOT:PSS films may be further enhanced by placing a highly reflective silver layer beneath the PEDOT:PSS film, providing a simple yet effective strategy for signal enhancement.

Keywords: SERS substrates, PEDOT:PSS, conducting polymers

1. INTRODUCTION

Since their discovery in the late 70s of the last century by Hideki Shirakawa, Alan MacDiarmid and Alan Heeger, conducting polymers have become a widely studied class of materials [1]. Due to their unique properties, including flexibility and high processability, conducting polymers are used in a wide range of applications that span from supercapacitors and photocatalysis to biomedical applications and gas sensing [2]. In addition, recent studies showed that conducting polymers are also a promising material for the development of platforms for surface-enhanced Raman scattering (SERS) spectroscopy. The pioneering works in this direction were conducted by G. Demirel et al. [3,4]. These authors demonstrated a significant Raman enhancement factor ($>10^5$) for the methylene blue (MB) probe molecule on an α,ω-perfluorohexylquaterthiophene (DFP-4T) film. Recently, it appeared that also poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is SERS active, which is connected with the molecular orbital delocalization induced by the transition of the PEDOT conjugated structure [5]. Due to the considerably lower price of PEDOT:PSS as compared to DFP-4T, this opens the way for the production of low-cost SERS active platforms.

However, Guo at al. [5] demonstrated in their study the SERS activity of PEDOT:PSS only for a relatively high concentration of MB (10^{-3} M), which is still too high for a sensitive detection. Because of this, this work re-investigates the SERS activity of PEDOT:PSS and introduces a simple and straightforward strategy to further enhance the SERS signal. This strategy is based on the application of a mirror-like layer, which has previously been shown to significantly improve the intensity of SERS peaks [6].

2. EXPERIMENTAL

2.1 Materials

Aqueous dispersion of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, F 020 formulation) was purchased from Ossila. Silver target (3-inch, thickness of 3 mm, declared purity of 99.99%) was supplied by Kurt J. Lessker. One-side polished Si wafers were purchased from MicroChemicals GmbH. Methylene blue (MB) was purchased from Sigma-Aldrich and was subsequently diluted in water to the desired 10^{-6} M concentration.

2.2 Samples preparation

The protocol for samples preparation is schematically depicted in **Figure 1**. First, Si wafers, used as substrates in this study, were cut into 1 cm x 1 cm pieces and cleaned by water and ethanol. One set of Si wafers was coated with sputter-deposited Ag films. The Ag deposition was performed in a stainless-steel vacuum chamber, equipped with a water-cooled, planar 3-inch magnetron, and pumped by a scroll (Edwards) and turbomolecular (Pfeiffer) pumps. The deposition was done in Argon (Linde, declared purity 99.99%) at a flow of 6 sccm, pressure of 3 Pa and magnetron current of 300 mA. The deposition time was 10 minutes and the distance between the samples to be coated and the magnetron was approximately 10 cm. Subsequently, PEDOT:PSS films were deposited by spin-coating of 100 μl of PEDOT:PSS aqueous dispersion onto Si wafers or Si wafers precoated with Ag film. The spin-coating was performed in open air at ambient temperature at a spinning speed of 2000 rpm for 60 seconds. Finally, samples were thermally cured at a hot plate at a temperature of 150 °C for 30 minutes, i.e., the conditions previously found to be optimal in terms of SERS activity of PEDOT:PSS [5].

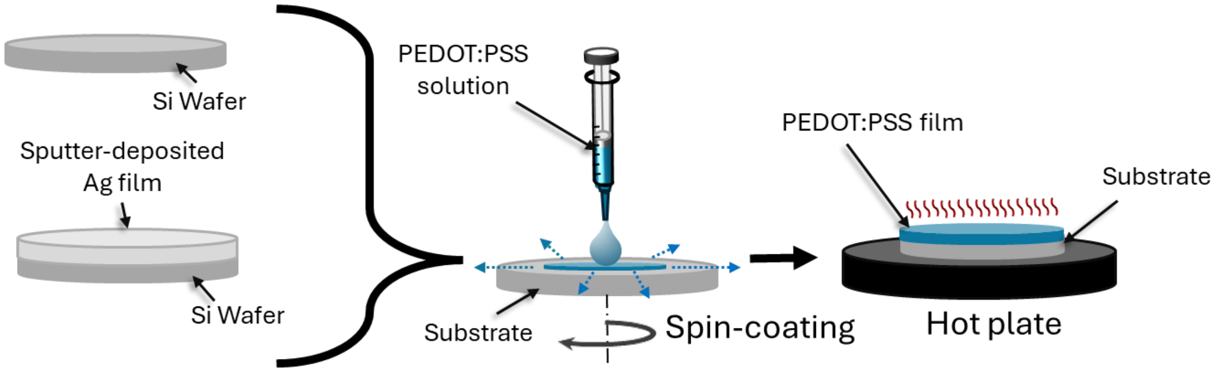

Figure 1 Schematics of the protocol used for preparation of PEDOT:PSS-based SERS active substrates

2.3 Samples characterisation and Raman measurements

The samples were characterised using scanning electron microscopy (SEM) with a field-emission microscope (JSM-7200F, JEOL) operated in secondary electron mode. The working distance was 10 mm, and the accelerating voltage was 15 kV. In addition, energy-dispersive X-ray spectroscopy (EDX) was used for mapping the elemental composition of produced samples using a JED-2300 detector (JEOL) attached to the SEM. A working distance was 10 mm, an accelerating voltage was 15 kV and a probe current was 7.475 nA.

Chemical structure was analysed by X-ray Photoelectron Spectroscopy (XPS). The XPS scans were acquired at a constant take-off angle of 90 degrees using Al Kα X-rays source (1486.6 eV, 200 W, Specs). Survey spectra were acquired for binding energies in the range of 0–1100 eV at a pass energy of 40 eV (dwell time 100 ms, step 0.5 eV). High-resolution XPS spectra were measured at a pass energy of 10 eV with 10 scans (dwell time 100 ms, step 0.05 eV) to obtain a higher spectral resolution and to lower the noise level. Spectral analysis was performed using CASA XPS software.

Raman spectra of PEDOT:PSS films deposited both onto Si wafers and Si wafers precoated with Ag were measured by means of a Raman system (LabRAM HR800, Horiba Jobin-Yvon) equipped with a confocal microscope connected to a spectrograph with an 800 mm focal length. A He-Ne laser (wavelength of 632.8 nm) was used as the excitation source. The laser power at the sample was ~0.3 mW. The spectra were subsequently detected by a Czerny–Turner spectrograph with a 300-groove-per-millimetre grating using a liquid nitrogen-cooled CCD detector. Accumulation time was 60 seconds.

The SERS activity of substrates was measured using MB as a probe molecule. The MB was deposited onto the PEDOT:PSS-based samples by their immersion into the MB solution for 120 minutes. The samples were then washed with distilled water and allowed to dry.

3. RESULTS AND DISUSSION

3.1 Samples characterisation

The first step was to characterise the spin-coated and thermally cured PEDOT:PSS films. As shown in **Figure 2a**, where a top-view SEM image of PEDOT:PSS coating is presented, the PEDOT:PSS film is inhomogeneous and has a granular-like structure. Concerning the chemical structure, XPS revealed the presence of oxygen (27 at. %), carbon (68 at. %), sulphur (4. at%) and sodium (1 at. %) (see **Figure 2b**). The presence of traces of sodium in the PEDOT:PSS originates from the dispersion preparation. In addition, the high-resolution XPS spectra of C 1s (**Figure 2c**) and S 2p **(Figure 2d**) peaks also revealed a structure typical of PEDOT:PSS. Namely, C 1s peak contains components that confirm the presence of C=C aromatic bonds in PEDOT (binding energy of 284.5 eV), the aliphatic C-C backbone of PSS (binding energy of 284.9 eV) and C-O/C-S and C=O/C=S bonds at binding energies of 286.7 eV and 288.7 eV [7]. In the case of S 2p, the lower binding energy peaks, at binding energies of 164.5 eV and 165.6 eV, correspond to the spin-split components of the sulphur atoms in PEDOT, while the higher binding energy peaks correspond to the sulphur atoms in the PSS [8].

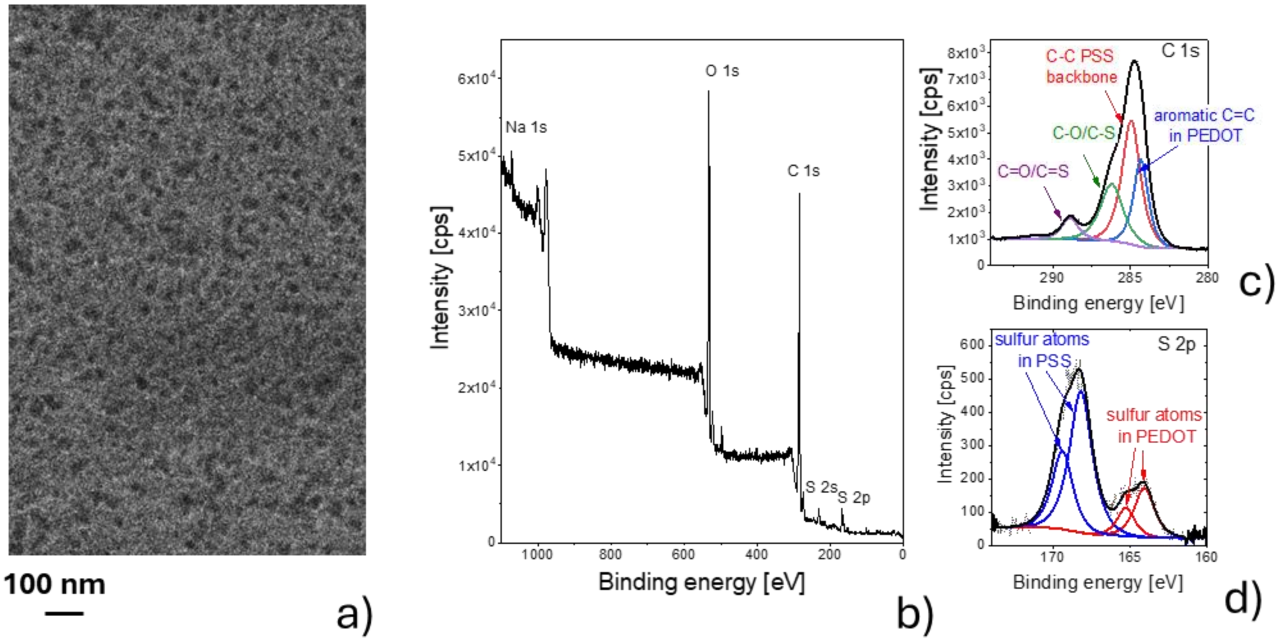

Figure 2 a) SEM image of PEDOT:PSS film. b) survey XPS spectra of PEDOT:PSS film and high resolution XPS spectra of c) C 1s and d) S 2p XPS peaks

Second, the PEDOT:PSS films were deposited onto Si precoated with an Ag layer. The comparison of the cross-section of both PEDOT:PSS film and the PEDOT:PSS film on Ag layer is presented in **Figure 3**. As can be seen, in both cases the thickness of PEDOT:PSS is approximately the same and close to 250 nm.

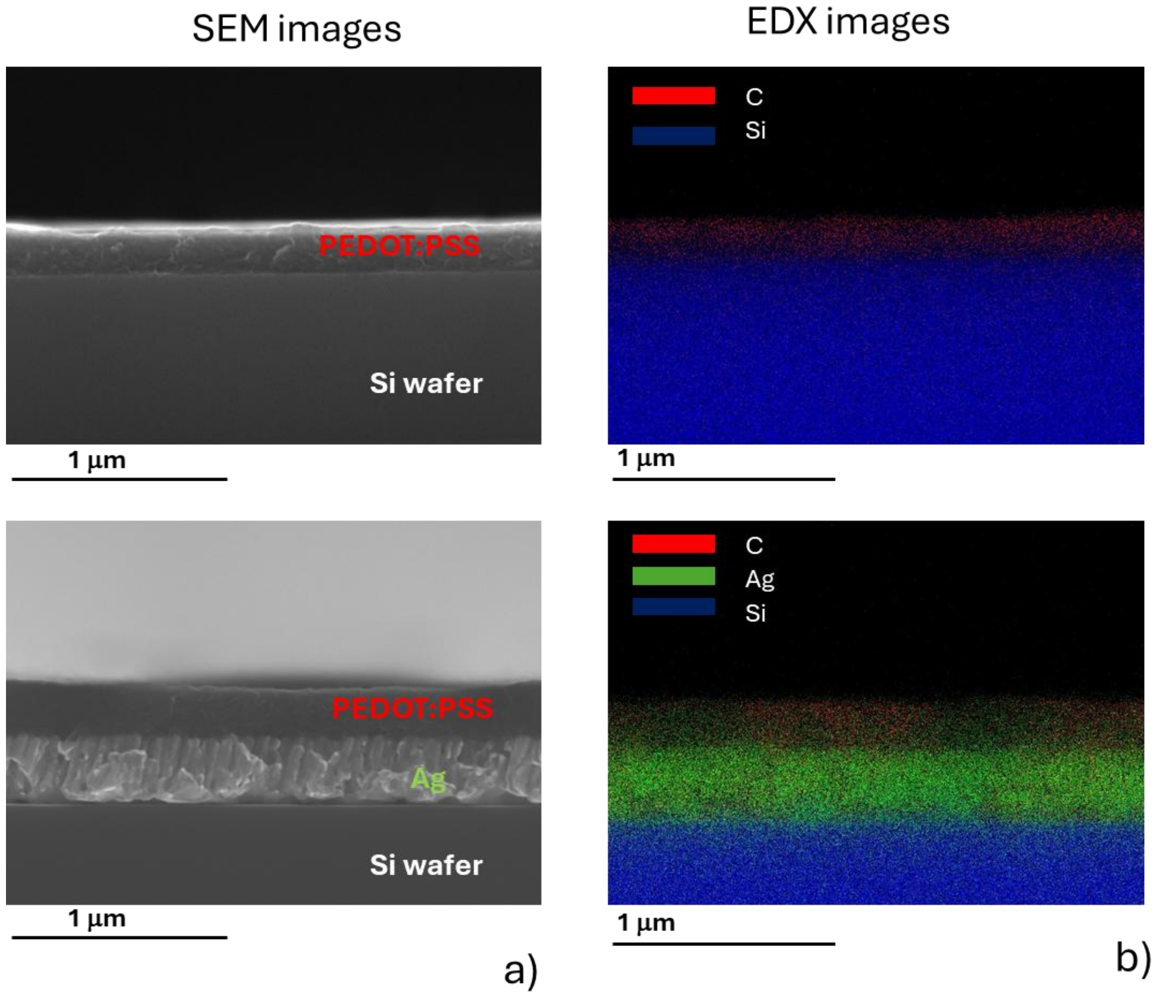

Figure 3 a) SEM images of cross-sections of PEDOT:PSS deposited onto Si wafer (top) and Si wafer pre-coated with Ag film (bottom). b) EDX elemental maps of C, Si and Ag that correspond to SEM images.

3.2 SERS activity

As can be seen in **Figure 4a**, the Raman spectrum of PEDOT:PSS, i.e., the spectrum measured without MB, is characterised by broad bands at about 991 cm^{-1} and 1430 cm^{-1} that are characteristic of PEDOT:PSS [9], and a sharp peak of Si at ~ 520 cm^{-1} that originates from the substrate. By application of an Ag layer beneath the PEDO:PSS film, an increase in intensities and appearance of new PEDOT:PSS Raman bands were observed. This signal enhancement reflects the fact that both the excitation laser and scattered light are reflected from the mirror-like Ag layer, which causes apparent enhancement of SERS activity of such a two-layer structure.

Next, after depositing MB onto PEDOT:PSS, new peaks appear in the spectra, among which the most intense is the peak at ~1624 cm^{-1} that corresponds to C-C aromatic ring stretching vibrations in MB [10]. At this point, it is worth mentioning that in comparison with the previous work [5], the concentration of detected MB is by 3 orders of magnitude lower in our case. Such substantially higher SERS-activity is most likely connected to the protocol of MB deposition; while MB was deposited by spin-coating from an ethanol solution of MB in the work

[5], the samples were left in an aqueous MB solution for 120 minutes in our case. Finally, the SERS signal of MB is further enhanced when an Ag base layer is used. This fact is highlighted in **Figure 4b**, where background-correct sections of SERS spectra of MB measured on both PEDFOT:PSS and PEDOT:PSS on Ag-coated Si are compared. It can be seen that the detected intensity is enhanced by a factor of 3. In addition, the acquisition of SERS spectra at 5 randomly selected positions on the samples revealed good spectral reproducibility that is below 5 % in both cases.

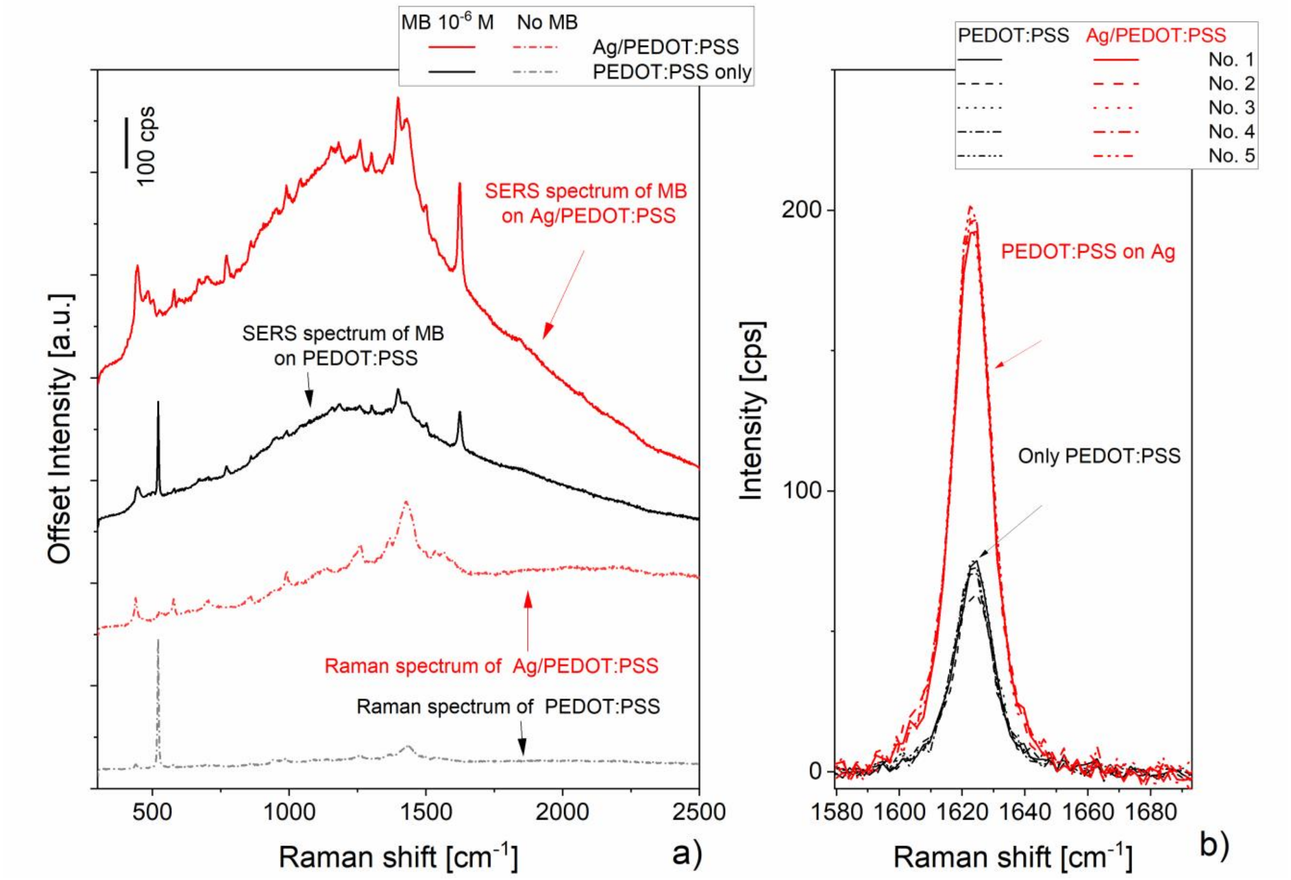

Figure 4 a) Raman spectra of PEDOT:PSS deposited on Si and Si pre-coated with Ag layer alongside of SERS spectra of MB on PEDOT:PSS deposited on Si and Si pre-coated with Ag layer. b) Background-corrected section of MB SERS spectra measured at 5 different spots on PEDOT:PSS deposited on Si and Si pre-coated with an Ag layer.

4. CONCLUSION

The key finding of this study is the remarkably high SERS activity of spin-coated and subsequently thermally cured PEDOT:PSS film. Furthermore, introducing a mirror-like Ag base layer beneath the PEDOT:PSS film provided an additional signal enhancement, utilising reflectivity to boost the SERS signal. This resulted in a threefold increase in the MB SERS signal compared to the Ag-free substrate, confirming the PEDOT:PSS/Ag two-layer structure as a highly promising platform for sensitive and reproducible chemical sensing.

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