Nanospectroscopy 2014; 1: 12–18 **DE GRUYTER** OPEN

Research Article **Open Access**

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Chemical stability of plasmon-active silver tips for tip-enhanced Raman spectroscopy

Abstract: Silver nanostructures are used in tip- and surface-enhanced Raman spectroscopy due to their high electric field enhancement over almost the entire visible spectral range. However, the low chemical stability of silver, compared to other noble metals, promotes silver sulfide and sulfate formation which decreases its plasmonic activity. This is why silver tips are usually prepared on the same day of the experiments or are disregarded in favour of gold that is chemically more stable. Since silver degradation cannot be avoided, we hypothesized that a protection layer may be able to minimize or control degradation. In this contribution, we report the successful preparation of 4-biphenylthiol and 4'-nitro-4-biphenylthiol self-assembled monolayers on silver tips in order to protect them against tarnishing and to investigate the effect on the life-time of the plasmonic activity. The electrochemically etched wire surface was probed via Raman spectroscopy and scanning electron microscopy. The best long term stability and resistance against corrosion was shown by a monolayer of 4-biphenylthiol formed from dimethylformamide which did not display any degradation of the metallic tip during the observed period. Here, we demonstrate an easy and straightforward approach towards increasing the chemical stability of silver TERS-active probes.

Keywords: Silver probes, SAM, Raman spectroscopy, scanning electron microscopy, tip-enhanced Raman spectroscopy, apertureless SNOM probes

DOI 10.2478/nansp-2014-0002
Received June 23, 2014; accepted November 3, 2014

1 Introduction

The quality and stability of the metallic nanostructure is a crucial issue in tip- and surface-enhanced Raman spectroscopy (TERS and SERS) experiments. It was shown that of the noble metals, silver provides the highest electric field enhancement over the entire visible spectral range [1]. However, silver sulfide (Ag_2S) and silver sulfate (Ag_2SO_4) are common atmospheric silver corrosion products that form on the probe surface. Their Raman bands, which appear around 188, 243, and 273 cm^{-1} for Ag_2S and 432, 460, 595, 623, 970 (strong), and 1079 cm^{-1} for Ag_2SO_4 [2], can coincide with spectral regions of interest such as the radial breathing mode of carbon nanotubes (CNT) [3]. It was also shown that the electric field enhancement decreases with the aging of the silver surface [4]; the thickness of Ag_2S increases over time as it is not a self-limiting process confined to the surface [5]. Thus, experiments with silver probes are almost exclusively performed on the day of the probe preparation as described in previous works [6]. Hence, a suitable tip coating of sufficient stability and with no or at least constant contribution to the Raman scattering intensity is desirable.

To the best of our knowledge, the Zenobi group [7, 8] have provided the only successful report in TERS literature regarding self-assembled monolayers (SAMs) utilized of ethanethiol and thiophenol on the tips. They employed ethanethiol SAMs to protect the surface of a silver probe for TERS in liquid conditions. The tip stability over time was not the aim of their studies, however, they showed that SAMs can provide protection against carbon and other tip contaminants. They also determined that the enhancement dropped by approximately a factor of 5 due to the coating [8].

Coatings should serve as a protection for tips and can be expected to replace contaminants. Compared to other protective coatings, SAMs with thiol anchor groups form

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particularly specific and long-term stable ultrathin films on noble metals. However, n-alkane thiols are prone to fast surface reconstruction upon change of the environmental polarity or mechanical stress as can be encountered in TERS experiments with atomic force microscopy. In previous studies, we investigated the self-assembly and SAM properties of biphenyl thiols [9]. The rigid mesogen allows a defined SAM on gold and silver surfaces to be formed [10] with a superior chemical and thermal stability [11] when compared to n-alkane thiols. Later studies showed that the rigid mesogen of biphenylthiol SAMs are ideal to stabilize various metal nanoparticles [12] during *in situ* formation, which demonstrates an effective SAM formation even at rough substrates or curved surfaces such as TERS tips. Here, we investigate the influence of several of such SAM coatings, dissolved in different solvents, on the chemical stability of electrochemically-etched silver tips for AFM.

2 Methods

Silver microwires (purity 99.9%) were electrochemically etched with DC pulses of 3 V in a KNO_3 solution. The etched wires were sonicated in an ethanol bath, rinsed with deionised water, and dried in a jet of nitrogen gas. The etched wires were immediately immersed in either a 4-biphenylthiol (BPT) or 4'-nitro-4-biphenylthiol (NBPT) solution in dimethylformamide (DMF) or ethanol (see Figure 1 for the chemical composition of the SAM precursors). The monolayers were left to assemble for 12 hours at 50 °C on a hot plate under ambient conditions, rinsed afterwards in DMF, and dried with a jet of nitrogen gas. The characterization of the etched wires was performed with a micro-Raman spectrometer (Horiba Labram HR800) in the spectral range from 80 to 1900 cm^{-1}. The Raman spectrometer used a diffraction grating of 600 l/mm, pinhole of 100 µm, and liquid nitrogen-cooled coupled-charged device (CCD) detector. The laser excitation wavelength was 514.7 nm with a power of 150 µW. The laser was focused with a 50xLWD objective on the tip apexes in order to assess the signal that could be observed while measuring in the tip-enhanced Raman spectroscopy configuration. The Raman spectra were normalized to the most intense Raman feature – at the laser cut-off and the ring C-C vibration at approx. 1590 cm^{-1}, for non-coated samples and coated samples, respectively. Raman mapping was performed under the same condition as the point measurements. For better visualization, the Raman maps images were smoothed. The step size was 1 µm and 0.5 µm for BPT and NPBT, respectively. The etched wires were examined directly after the SAM formation and after one week in order to identify the effect on the chemical stability of the tips. The probes were stored under ambient conditions between the experiments. The surface morphology was characterized by a scanning electron microscopy (SEM, FEI NovaNanoSEM 200) in secondary electron mode with a beam current of 5 kV.

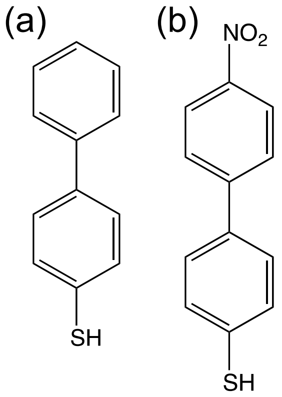

Figure 1: Chemical composition of self-assembled monolayers (a) 4-biphenylthiol (BPT) and (b) 4'-Nitro-4-biphenylthiol (NBPT).

3 Results

3.1 Micro-Raman spectroscopy

The electrochemically etched wires were probed by Raman spectroscopy. A batch of several etched wires coated with SAMs was prepared together with etched wires with no protective coating, used as controls to monitor the influence of the coating in the long-term stability. All wires were studied immediately after the SAM coating and the etching of controls on the same day. After several days since etching, the control wires show a typical intensity increase in silver sulfide bands in the low frequency range 180 – 300 cm^{-1} (see Figure 2). The silver sulfate band with the most intense and sharp feature at 970 cm^{-1} was not observed. Although the two silver-sulphur phases were investigated elsewhere, the reasons for the appearance of Ag_2S and not Ag_2SO_4 are beyond the scope of the present work. The remaining bands can be attributed to SERS spectral fluctuations of carbonaceous contamination [13], which decrease in intensity with the wires aging.

The Raman spectra after monolayer assembly are shown in Figure 3-Figure 5 in the fingerprint region (see Figure 3c for the assignment of the vibrational modes [14]). Comparing the spectra of wires with the BPT-SAM (immersed in DMF) coating to non-coated wires, the

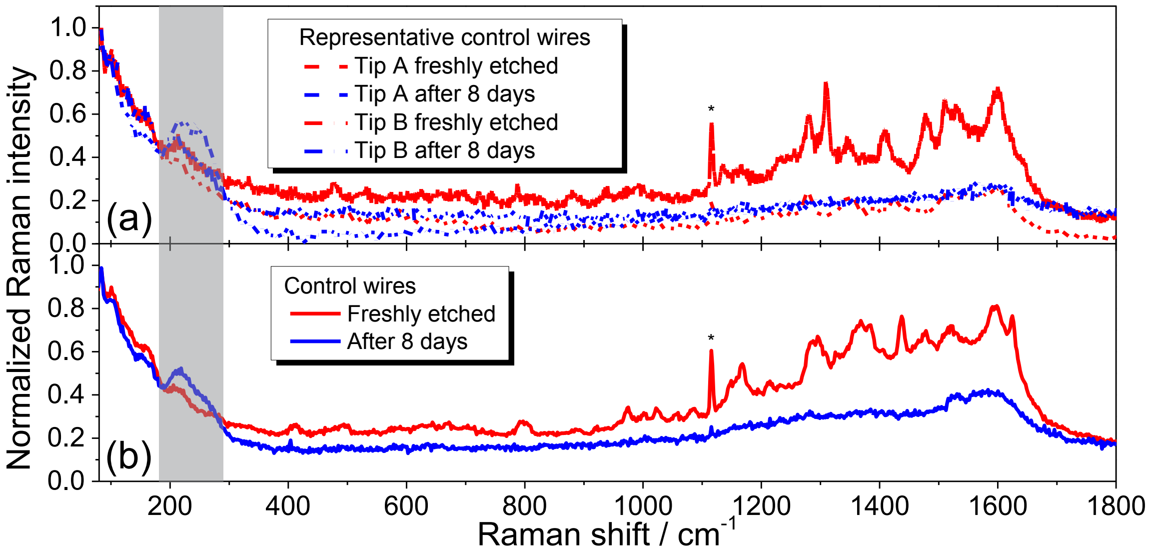

Figure 2: Representative Raman spectra of two freshly etched wires and wires after 8 days of aging (a) and averaged Raman spectra of all freshly etched and after 8 days control wires (b). In area in grey colour, the Raman bands can be attributed to the silver corrosion process. The asterisk indicates peak of parasitic visible light.

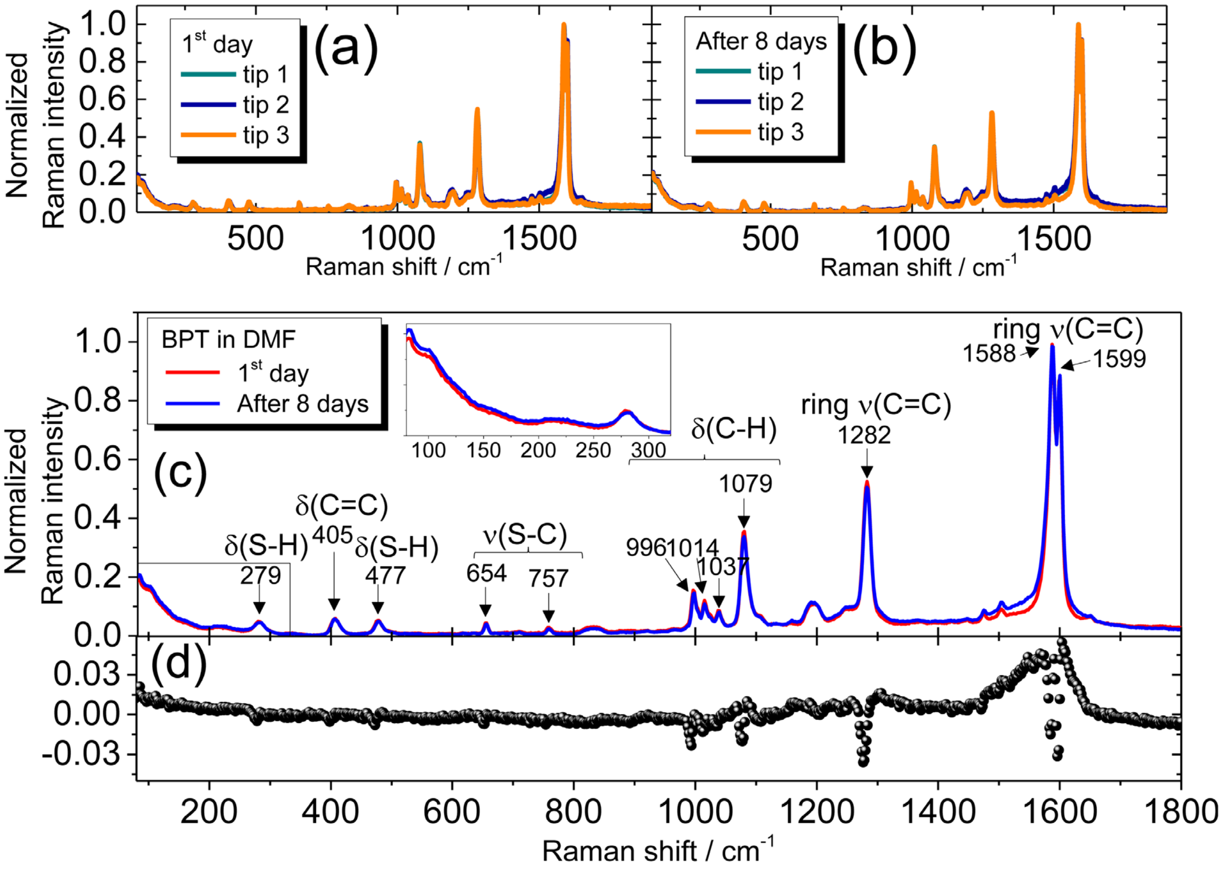

Figure 3: (a) Raman spectra of electrochemically etched silver wires with a SAM coating of 4-biphenylthiol (BPT) immersed in DMF. Several representative spectra of SAM protected wires measured on the first day immediately after assembly, (b) after 8 days, (c) comparison of averaged spectra of the first day (red line) and on the 8th day (blue line), (d) and difference spectrum of averaged spectra.

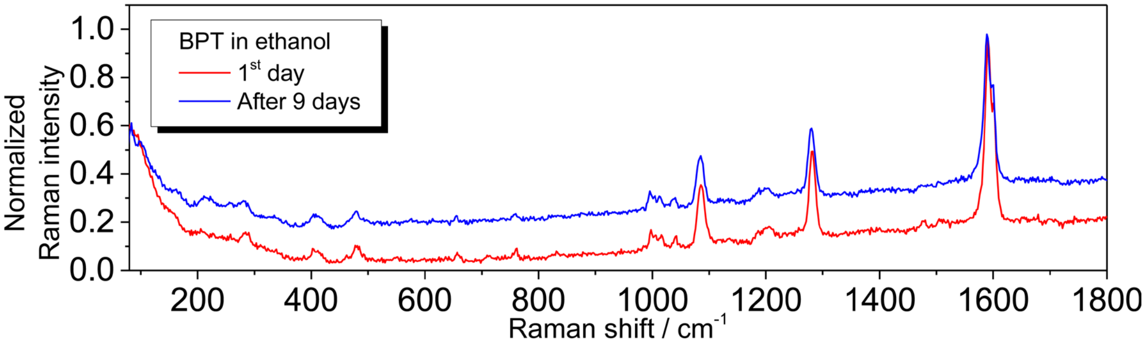

Figure 4: Comparison Raman spectra of averaged spectra of the first day (red line) and after 9 day (blue line) of electrochemically etched silver wires with a SAM coating of ethanol-immersed 4-biphenylthiol (BPT) with a difference spectrum of the averaged spectra as insert.

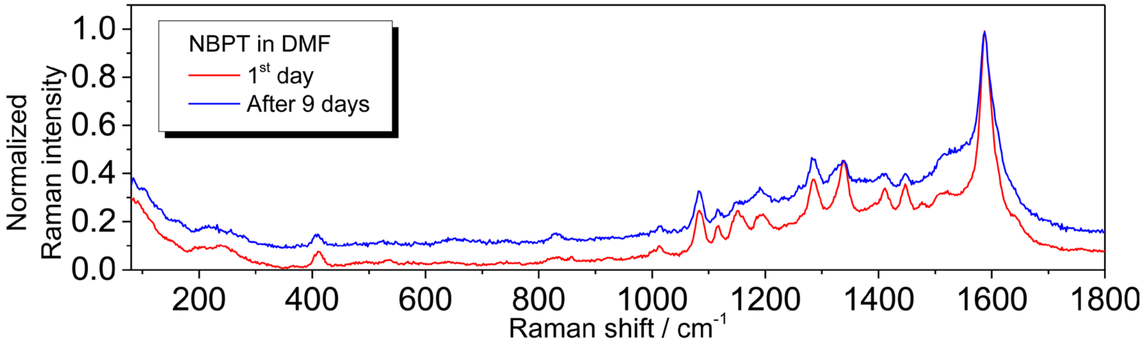

Figure 5: Comparison Raman spectra of averaged spectra of the first day (red line) and after 9 day (blue line) of electrochemically etched silver wires with a SAM coating of DMF-immersed 4’-nitro-4-biphenylthiol (NBPT) with a difference spectrum of the averaged spectra as an insert.

coated wires do not display any intensity increase in the region associated with silver sulfide or silver sulfate bands. There is a small observable change after several days in the Raman spectra of the wires with SAM coating that is introduced by carbonaceous contamination as evidenced by the difference spectra (see the inset of Figure 3). The Raman spectra obtained with the SAM coating of BPT immersed in ethanol is shown in Figure 4. Unfortunately, after several days the spectra display signs of silver sulfide formation in the low frequency region in addition to an increase in background. As shown in Figure 5, DMF-immersed NBPT-SAM coated wires are resistant towards further corrosion although an increase in background, attributed to carbonaceous contamination (Figure 5), still occurs. It is important to note that the absolute carbonaceous Raman intensity from the control wires was 1-2 orders of magnitude lower than the signal originating from the SAM coating.

The Raman spectroscopy imaging results displayed in Figure 6 show the uniformity of the coating on the tip surface. The Raman intensity images are plotted for the most intense Raman band of BPT and NBPT at 1589 cm^{-1}. At the tip apex we observed localized Raman enhancement for both BPT and NBPT-coated tips. By comparison, the number of molecules at the tip end is much smaller than along the tip shaft simply due to the smaller surface area at the apex. However, we can observe the maximum signal at the apex as can be explained by the higher electric field enhancement at the plasmonic structure singularities, *i.e.* tip apex. Therefore, the relatively high intensity at the tip end compared to the intensity along the tip suggests a good plasmon activity of the silver tips under 514.7 nm excitation [15].

3.2 Scanning electron microscopy

In order to investigate the surface morphology of the electrochemically etched wires, scanning electron microscopy was employed. The morphology of a silver etched wire is displayed in Figure 7 with an enlarged wire apex, which typically had sizes below 50 nm. In comparison, the micrographs of wires with SAM protection showed very similar surface morphology (see Figure 7c, d).

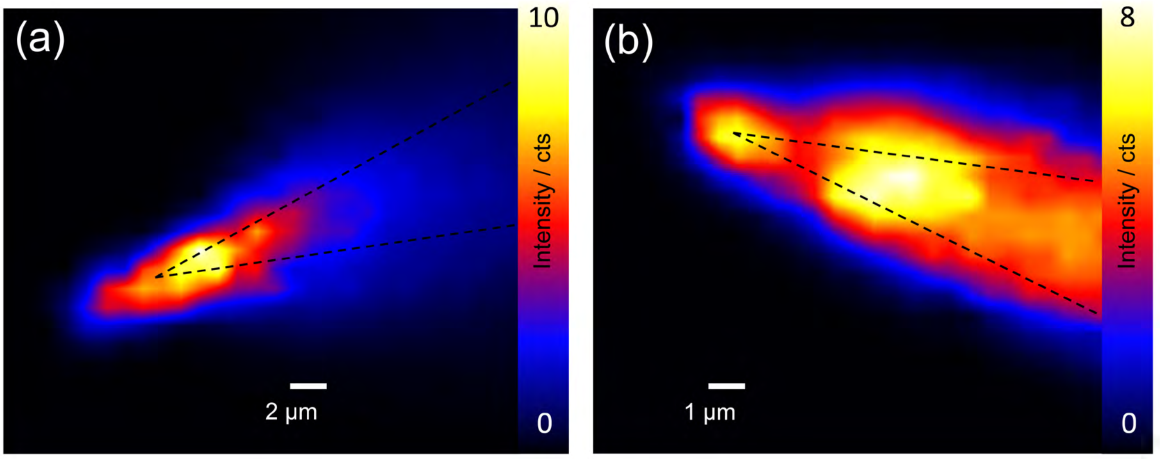

Figure 6: (a) Raman intensity mapping of the 1589 cm^{-1} band of the electrochemically etched wire apex with SAM coating of BPT, (b).and NBPT

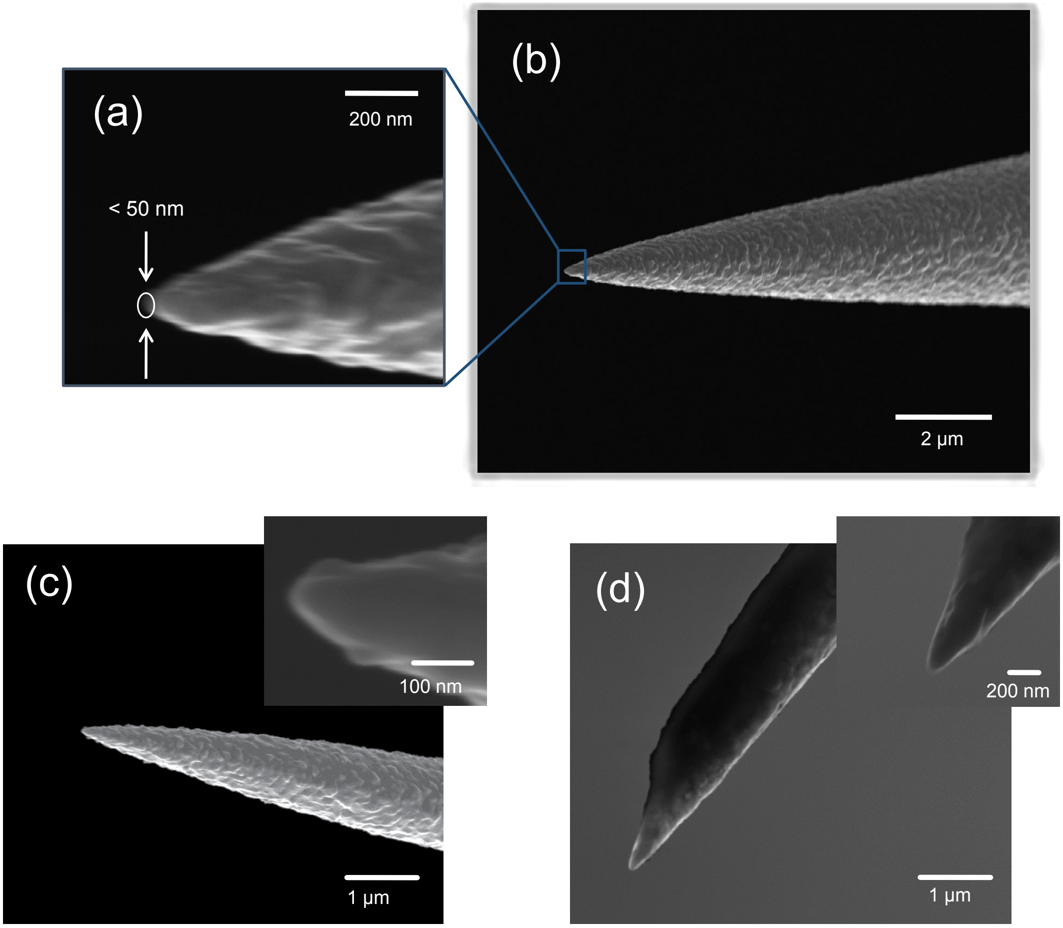

Figure 7: Typical SEM micrograph (b) of an electrochemically etched silver probe, (a) with enlarged tip apex, (c) a wire apex coated with a monolayer BPT (d) and NBPT – both immersed in DMF – with insets of higher magnification. From the SEM micrographs no change in surface morphology was observed.

4 Discussion

As can be seen from the uncoated tips in Figure 2, the amorphous carbon features are subsiding over time whereas the silver sulfide bands are increasing in intensity. We assume that during the corrosion process the silver sulfide replaces the amorphous carbon on the tip surface. Although SAM formation on well-defined surfaces was demonstrated in our previous works, the coating of heterogeneous surfaces such as that of TERS tips may be affected by the tip curvature and roughness. Therefore, we needed to assess whether or not SAM formation on the silver tips does in fact take place and whether we achieve a full SAM tip coverage. The Raman spectroscopy results give a good indication of the SAM formation, in particular the prolonged chemical stability achieved for coated samples in comparison to non-coated ones. We believe that this is an indication of a passivation effect due to SAM formation. Based on our previous investigation of biphenylthiol SAM formation on curved surfaces [12], we can conclude that the SAM coating was achieved in all three cases investigated here. The SAM formation was confirmed by the Raman spectroscopy imaging results in Figure 6. If large-area patches with no SAM formation had occurred, then these regions should have been visible in the Raman mapping results as the laser spot size is around 1 µm. SAMs with different chemical structure and in different solvents were investigated in order to find the best combination for tip protection. As expected, we found that the chemical stability of the silver tips differed. The SEM investigations showed that the etched wires have very similar surface morphology with and without the protective layer. In addition, the linear background increase in the Raman spectra can be explained by a carbonaceous contamination which is a common issue for silver tips and surfaces [16]. This is clearly proven by the appearance of amorphous carbon bands, which are typically broad around 1300 and 1600 cm^{-1}, as can be observed in the difference spectra of the SAM coated tips on the first day and after aging. In the case of NBPT SEM assembled in DMF, monolayer formation protected the probe against sulfidation. However, the increase in background at higher energies could imply the presence of carbonaceous contamination. BPT diluted in ethanol might have not formed a complete layer since silver sulfide formed on the probe surface as evidenced from the Raman spectra in Figure 3d. The most stable coating proved to be a BPT SAM assembled in DMF solution. This coating showed nearly no changes during the observed period of 8-9 days, prolonging the tips lifetime and plasmon activity. This conclusion is in agreement with the recent report from Bortchagovsky *et al.* [7] who used SAM on tips as an internal reference for TERS. In our case, the bands from C-C bonds show similar Raman intensity after 9 days as they had on day 1 evidencing the TERS activity of the probes, as well as the tips' time and chemical stability.

The next steps in the development of such probes will be testing them in the tip-enhanced Raman spectroscopy experiment and compare the enhancement of uncoated and coated tips. In addition, the coating wear-off and possible sample contamination by the probe coating needs to be assessed.

5 Conclusion

We successfully prepared electrochemically etched silver wires with a protective self-assembled monolayer of either 4-biphenylthiol or 4'-nitro-4-biphenylthiol. We demonstrated that these SAMs can be used to prolong the life-time and stability of silver tips used in tip-enhanced Raman spectroscopy. The protective coating on the probes induced no structural changes to the metallic surface. The longest stability was demonstrated by the coating with 4-biphenylthiol assembled in dimethylformamide. We are confident that this work contributes to the establishment of silver tips for near-field and plasmonic applications.

Acknowledgements: This work was funded by the Cluster of Excellence “Center for Advancing Electronics Dresden“ (cfaed) and by the DFG-Research Unit 1713 “Sensoric Micro- and Nanosystems”.
We would like to thank Dr. Steffen Schulze and Professor Michael Hietschold (Solid Surfaces Analysis, Technische Universität Chemnitz) for support with the scanning electron microscopy experiments. The authors acknowledge COST Action MP1302 NanoSpectroscopy

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