Surface modified high rectification organic diode based on sulfonated poly(aniline)

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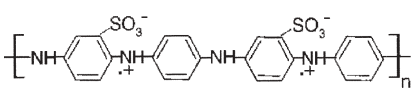
In this paper, we present a new method that combines surface modification of indium-tin oxide (ITO) and electropolymerization to prepare thin, sulfonated poly(aniline) (SPAN) films with good surface coverage. The surface modification enhances the growth of the SPAN film resulting in a better rectification signal than for SPAN films polymerized on unmodified ITO substrates. The films were characterized by FTIR, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The sulfonation degree of SPAN was determined to 29% by X-ray photoelectron spectroscopy (XPS). UV-VIS spectroscopy shows that the pH sensitivity of SPAN is suppressed due to sulfonation of the polymer backbone. It is also shown that conversion of the SPAN film to the emeraldine salt (ES) form after polymerization is crucial for obtaining a high rectification signal. This is an important practical aspect in the preparation procedure of organic electronic devices.

1 Introduction

Sulfonated poly(aniline) (SPAN) is classified as a self-doped conducting polymer (CP) due to the sulfonic (SO_3^-) groups, which are covalently bound to the polymer backbone (Scheme 1).[1,2] It has been reported that the acid–base chemistry of the strongly pH-sensitive poly(aniline) (PANI) is influenced by the sulfonation. The electroactivity of SPAN is therefore retained even in neutral solutions at pH < 7.5.[2] The main reason for the pH insensitivity is the interaction between the negatively charged sulfonic groups and protons of the SPAN backbone. This interaction keeps SPAN in the conducting emeraldine salt (ES) form and prevents it from becoming deprotonated at neutral pH.

SPAN has been used in many different areas. For example, Shimizu *et al.*[3] have proposed a method to chemically prepare SPAN with ammonium peroxydisulfate (APS) from sulfonic acid-substituted aniline (3-aminobenzenesulfonic acid, *e.g.* metanilic acid). They identified the usefulness of self-doped SPAN in lithography. On the other hand, Barbero *et al.*[4] have suggested that SPAN can be used as cation-insertion electrodes for battery applications. Different synthetic routes for preparing SPAN have been published since the early paper of Yue and Epstein.[1] In their work, the sulfur groups were covalently attached to the PANI backbone by exposing the polymer to sulfuric acid fumes. A 100% sulfonation degree of thin SPAN films has later been achieved by electrochemical homopolymerization of metanilic acid in 4 : 1 acetonitrile–water mixtures.[5] The obtained SPAN film was, however, soluble in both organic and aqueous solvents. Considering practical applications, the solubility of SPAN can be overcome by copolymerization of aniline and metanilic acid (1 : 10), which usually results in a sulfonation degree of 25%.[6,7] It should be noted that Scheme 1 shows a simplified chemical structure of SPAN with a sulfonation degree of 50%.



Scheme 1 Chemical structure of sulfonated poly(aniline) (SPAN) with a sulfonation degree of 50%.

Both PANI and SPAN have been utilized in high rectification devices[8] and applied as the hole-transporting layer in organic solar cells.[9–12] Similar current–voltage (I–V) behaviour was observed for solar cells having either SPAN or poly(3,4-ethylenedioxythiophene) (PEDOT) as the hole-transporting layer. PEDOT prepared with polystyrenesulfonic acid (PSS) as the dopant ion (PEDOT:PSS) is commonly used as a hole-transporting layer in organic solar cells.[9,10,13,14] It was also recently shown that SPAN improves the rectification of electronic devices and that the contact resistances of SPAN|metal (Al, Au, Cu) interfaces are lower than for PEDOT:PSS.[8,14]

In this paper, we report that the electrochemical film growth of SPAN can be enhanced by surface modification of the indium-tin oxide (ITO) substrate (Scheme 2). Regio-regular poly(3-hexylthiophene) (RR-P3HT) was spin-coated on top of the SPAN layer. We show that this substrate modification is essential for obtaining high device rectification, which is much better than the rectification reported for similar SPAN-containing devices with unmodified substrates.

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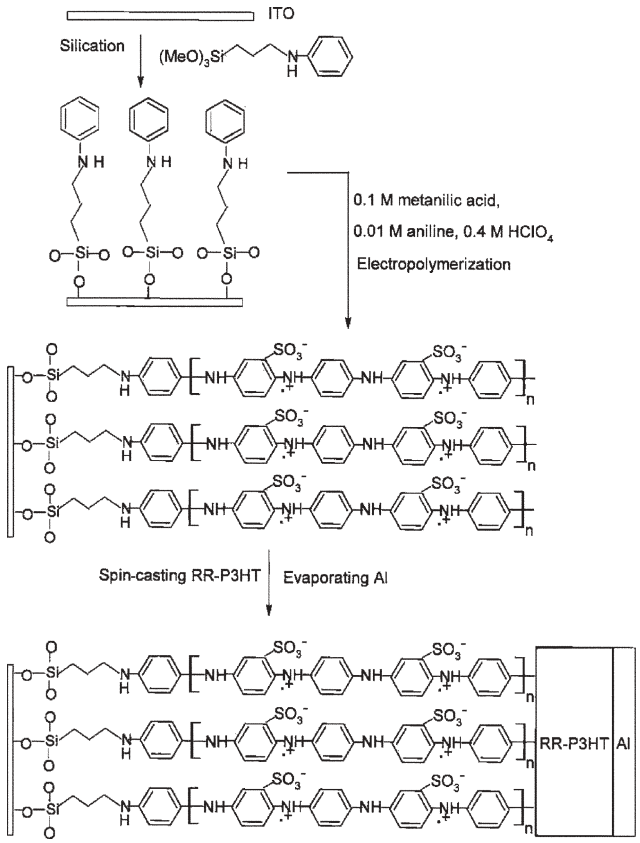

Scheme 2 Schematic view of the preparation procedure of the MITO/SPAN/RR-P3HT/Al device. MITO: aniline silane modified indium-tin oxide (ITO) substrate; SPAN: sulfonated poly(aniline) (sulfonation degree: 50%); RR-P3HT: regio-regular poly(3-hexylthiophene).

2 Results and discussion

2.1 Electropolymerization

The electropolymerization of the SPAN copolymer was carried out by cyclic voltammetry (CV). The cyclic voltammograms obtained during electropolymerization (last cycle) of 3-amino-benzenesulfonic acid (3-ABA) and aniline (concentration ratio: 10 : 1) on the unmodified ITO and the ITO substrate modified with aniline silane (MITO) are shown in Fig. 1. The surface modification is described in detail in the Experimental section. The higher current response observed in the CV of the SPAN film on the MITO substrate indicates that the film growth is enhanced on MITO. This is probably due to a more homogenous nucleation process and film growth taking place on the MITO substrate.

2.2 SEM and AFM measurements

The results of the scanning electron microscopy (SEM) measurements are shown in Fig. 2a–c. A compact and granular surface structure is obtained on MITO (Fig. 2c), whereas the electropolymerization on unmodified ITO results in an inhomogeneous surface morphology (Fig. 2b). The piranha-treated (see Experimental section) unmodified ITO substrate is shown for comparison in Fig. 2a.

Atomic force microscopy (AFM) measurements also clearly reveal the difference in surface coverage between the SPAN

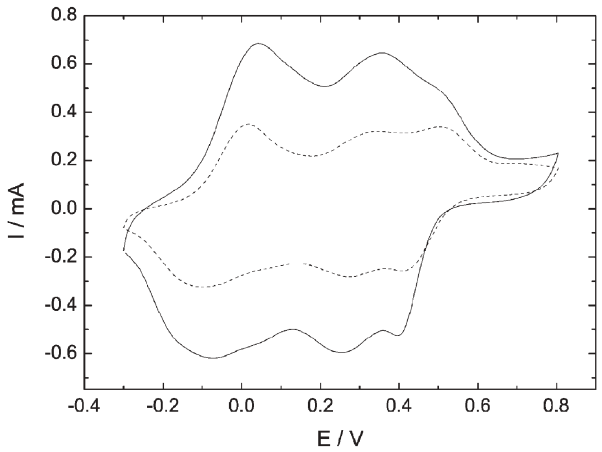

Fig. 1 Cyclic voltammograms obtained during copolymerization of 0.1 M 3-aminobenzenesulfonic acid (metanilic acid) and 0.01 M aniline in an aqueous solution of 0.4 M $HClO_4$ on unmodified ITO (dashed line) and MITO (solid line). The potential was cycled between -0.3 and 0.8 V (50 cycles) with a scan rate of 50 mV s^{-1}. The last cycle is shown in the figure.

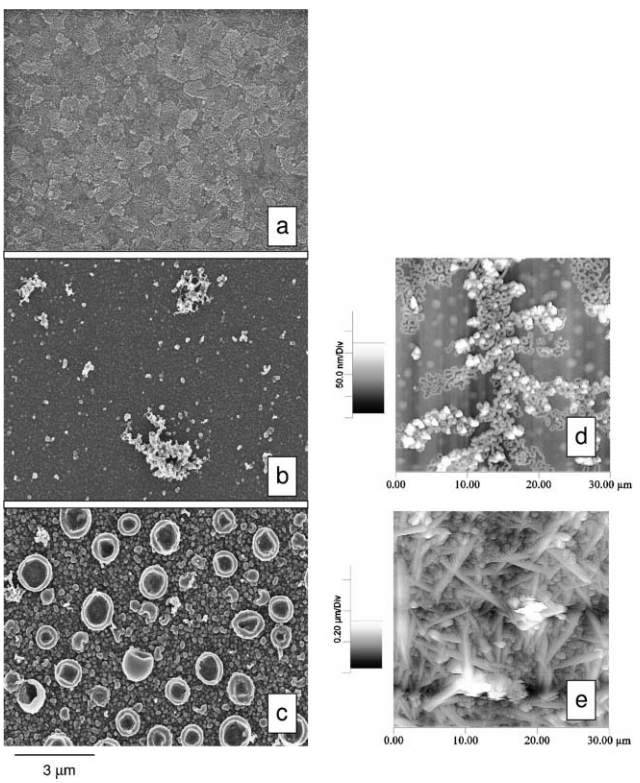

Fig. 2 SEM images of (a) the unmodified ITO substrate, and the SPAN film electropolymerized on (b) unmodified ITO and (c) MITO. The AFM images of SPAN on unmodified ITO and MITO are shown in (d) and (e), respectively. The headings of the AFM height profiles (50.0 nm/DIV and 0.20 μm/DIV) indicate that height profiles are divided in increments of 50 nm and 0.20 μm, respectively.

films that were polymerized on ITO and MITO (Fig. 2d and 2e). The unmodified ITO substrate was not always covered with a uniform SPAN film and often the bare ITO substrate was visible in the AFM images (Fig. 2d). Most of the SPAN film is scattered as clusters. In the regions between the

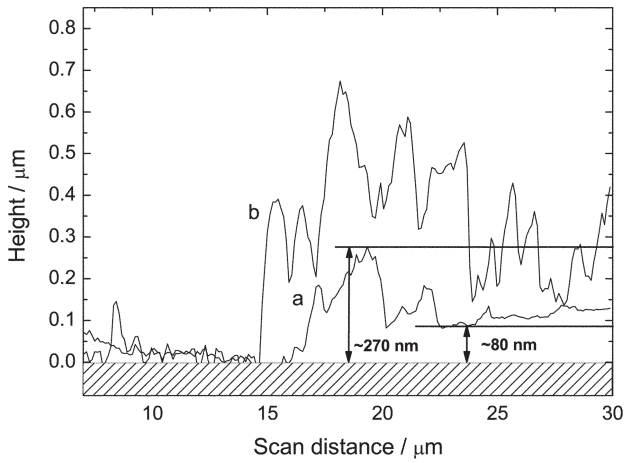

Fig. 3 AFM height profiles of the SPAN film on (a) unmodified ITO and (b) MITO.

clusters, the unmodified ITO substrate was only partially covered with the SPAN film having an average thickness of *ca.* 80 nm (Fig. 3; height profile: a). In the case of the SPAN film prepared on MITO (Fig. 2e), the surface morphology of the film is completely different from SPAN polymerized on ITO. The SPAN film shows a regular, rod-like surface structure extending over the whole film surface. The surface morphology of the SPAN film on the MITO substrate is much more regular with a highly improved surface coverage and with only few spots where the bare ITO substrate can be observed in the AFM images. The average thickness of the SPAN film on MITO is *ca.* 270 nm (Fig. 3; height profile: b) with some very rarely occurring bigger clusters.

2.3 XPS measurements

It is very important for the performance of the final device that the SPAN layer is in the electrically conducting ES form when the RR-P3HT layer is applied on top of it. The influence of two different surface post-treatment procedures on the oxidation state of SPAN was therefore studied with X-ray photoelectron spectroscopy (XPS): (a) the SPAN film was rinsed with deionized water (pH *ca.* 5.5) after completing the electropolymerization at −0.3 V, and (b) the SPAN film was polarized at a positive potential of 0.3 V for 10 min and then rinsed with 0.4 M $HClO_4$ in order to avoid the transformation of the film from the ES to the non-conducting emeraldine base (EB) form. The N 1s spectra of the two differently treated SPAN films are shown in Fig. 4. Three different peaks could be distinguished for the SPAN film that was rinsed with deionized water directly after completing the electropolymerization at −0.3 V (Fig. 4a). These peaks corresponds to benzenoid amine groups (–NH–; 399.6 eV; 75% of the total XPS peak area), cationic nitrogen atoms (polarons and bipolarons; 400.9 eV; 18%) and localized protonated amine groups ($–NH_2^+–$; 402.3 eV; 7%).[15–17] The stronger electron localization makes the binding energy of these protonated amine units higher. The strong XPS signal from the benzenoid amine groups (399.6 eV) in Fig. 4a confirms that most of the SPAN film was in the electrically non-conducting leucoemeraldine base (LEB) form after completing the

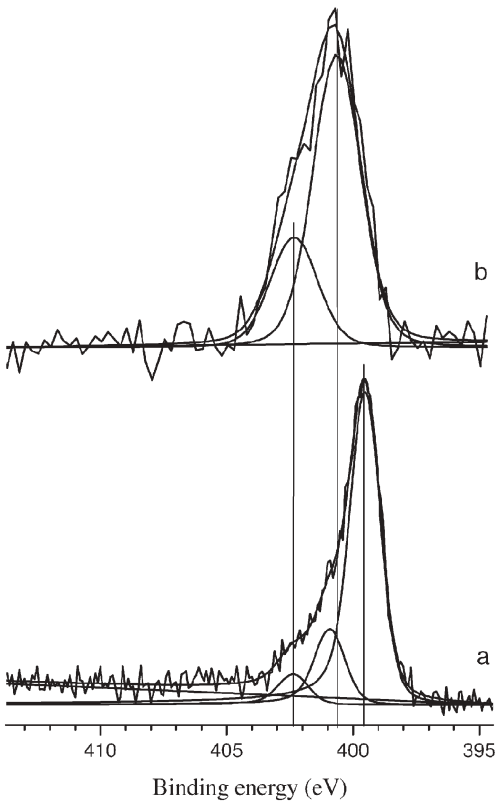

Fig. 4 XPS N 1s spectra of the MITO/SPAN film, which was (a) rinsed with deionized water after completing the electropolymerization at −0.3 V, and (b) kept at 0.3 V (10 min) and washed with 0.4 M $HClO_4$ after the electropolymerization.

electropolymerization at −0.3 V. Only a minor fraction of the film was in the electrically conducting ES form (400.9 eV) and no signal related to the quinoid imine groups (–N=) at 398.2 eV could be observed in the XPS spectrum.[16,17] This indicates that the rinsing of the SPAN film with deionized water after completing the electropolymerization at the negative potential of −0.3 V had a minor influence on the electrical conductivity of the film. On the other hand, the XPS spectrum of the SPAN film obtained after the combined polarization at 0.3 V (10 min) and acid rinsing, shows that the film had completely converted from the electrically non-conducting LEB to the electrically conducting ES form (polarons and bipolarons; 400.6 eV; 73%) (Fig. 4b). Simultaneously, the benzenoid amine groups (399.6 eV) became protonated (402.4 eV; 27%). This shows the importance of the correct post-treatment of the SPAN film at a sufficiently positive potential before spin-coating the RR-P3HT layer on top of it. After keeping the SPAN film at a positive potential, it is equally important, in contrast to treatment at a negative potential, not to rinse the SPAN film with deionized water in order to avoid the ES to EB conversion of the film. After the acid treatment a chlorine residue (Cl $2p_{3/2}$ at *ca.* 199.9 eV) originating from $HClO_4$ was present on the sample surface.

The sulfur 2p line at 167.7 eV (data not shown) was obtained at a relatively good resolution and it was confirmed that sulfur was present in a single oxidation state in all samples. The XPS

measurements showed also that the sulfonation degree of the polymer backbone was 29% (determined from the sulfur to nitrogen ratio).

2.4 FTIR and UV-VIS measurements

The FTIR spectra also confirm that an improved growth of the SPAN film takes place at the MITO substrate, resulting in a better surface coverage in comparison with unmodified ITO. Significantly higher absorbances were observed in the FTIR spectrum of the SPAN film on MITO than for SPAN on unmodified ITO. The FTIR spectra of the SPAN film on MITO, which was treated at 0.3 V (10 min) and washed either with 0.4 M $HClO_4$ (pH *ca.* 0.4) or deionized water (pH *ca.* 5.5), are shown in Fig. 5. The peaks at 1616, 1569, 1560, 1498, 1339, 1315, 1262, ~1160, ~1140 and ~970 cm^{-1} in spectrum (a) and the peaks at 1583, 1506, 1376, 1340, 1304, 1259, 1242, 1177, 1147, 807 and 745 cm^{-1} in spectrum (b) are characteristic of the ES and EB form of PANI, respectively. The assignments of these peaks were reported in detail by Ping *et al.*[18,19]

The peak at *ca.* 1094 cm^{-1} in spectrum (a) originates from the ClO_4^- counterions.[20] The ClO_4^- counterions were expelled from the SPAN film when it was converted to the EB form and can therefore not be seen in spectrum (b). The strong peak in spectrum (b) at *ca.* 1015 cm^{-1}, originating from the strectching of S=O groups in the aromatic ring structure,[21,22] verify that the sulfonic groups are covalently bound to the polymer backbone. Electrostatically bound SO_3^- groups, functioning as charge balancing counterions in the doping process of SPAN, would leave the polymer film together with the ClO_4^- during the conversion of the SPAN film from the ES to the EB form.

The pH sensitivity of the SPAN film was studied in more detail between pH 2 and 12 with UV-VIS spectroscopy (Fig. 6). The measurements were conducted in the transmission mode and pH-dependent changes of the entire SPAN film could therefore be followed. The peak at *ca.* 410 nm (pH 2) and the increasing absorbance at $\lambda > 900$ nm (charge carrier 'tail' indicating delocalized charge distribution) in the UV-VIS spectra in Fig. 6 are related to polaron band transitions (ES form),[23] whereas the peak at 624 nm is attributed to the EB form of SPAN.[24,25] The UV-VIS spectra in Fig. 6 reveal that the SPAN copolymer is rather pH-insensitive between pH 2 and 7 with only minor pH-dependent changes taking place in the UV-VIS spectra. The most pronounced changes occur at pH > 8. These results are in good accordance with previously published results on the pH sensitivity of SPAN.[2] FTIR measurements (Fig. 5; spectrum b) indicate, however, that the surface of the SPAN film is more easily converted to the EB form than the bulk of the film. It should be noted, that the penetration depth of the light beam in the FTIR measurements was considerably lower than the SPAN film thickness.

2.5 Rectification response

The introduction of an intermediate SPAN or PEDOT:PSS layer in organic electronic devices will increase the rectification current when the device is positively biased. It has been shown that the potential barrier between the metal electrode and PEDOT:PSS layer is very low[8,14,26,27] and thus the potential barrier is mainly determined by the PEDOT:PSS|RR-P3HT interface. Similar I–V characteristics were found for SPAN and PEDOT:PSS.[2] Fig. 7a (filled circles) shows that the I–V characteristics of the unmodified ITO/SPAN/RR-P3HT/Al device with a rectification value of *ca.* 1×10^2 are in good accordance to the behaviour reported by Roman *et al.*[9] In the case of the surface modified MITO/SPAN/RR-P3HT/Al device, however, the rectification is highly improved to a value of *ca.* 1×10^4 (Fig. 7b, filled circles). In both cases, the SPAN was conditioned to the ES form prior to deposition of RR-P3HT and Al, and can thus be considered as an Ohmic contact to the ITO and MITO substrates.[27] This is further verified by an experiment where the SPAN film was transferred to the EB form by conditioning at pH 12 prior to the deposition of the RR-P3HT and Al layers. This resulted in a strongly suppressed rectification response from the device, as shown in Fig. 7a and 7b (open circles).

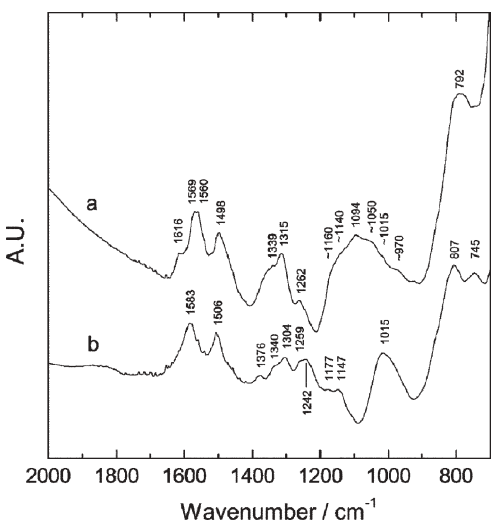

Fig. 5 FTIR spectra of the (a) ES and (b) EB forms of SPAN on MITO. The SPAN films were treated at 0.3 V (10 min) and washed either with (a) 0.4 M $HClO_4$ (pH *ca.* 0.4) or (b) deionized water (pH *ca.* 5.5) before the FTIR measurements were conducted.

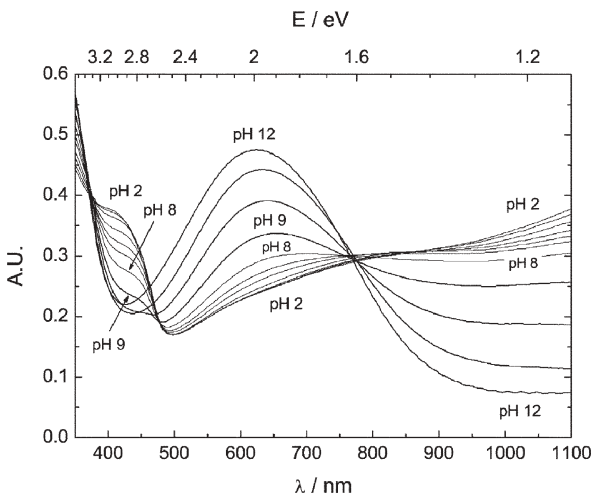

Fig. 6 UV-VIS spectra of the MITO/SPAN film measured in pH buffer solutions with pH 2–12 (ΔpH = 1; equilibration time: 30 min).

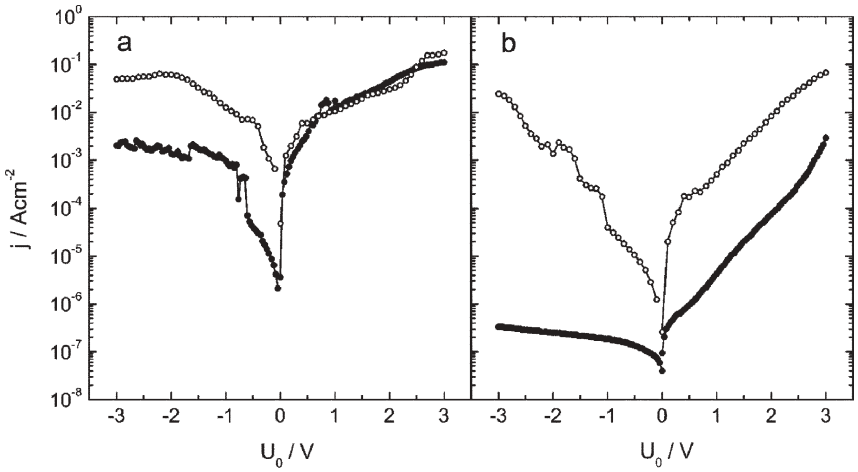

Fig. 7 Current–voltage characteristics of SPAN-based diodes prepared on (a) unmodified ITO and (b) MITO, where SPAN is either in the (●) electrically conducting (ES) or (○) non-conducting form (EB) form. Diode configuration: substrate/SPAN/RR-P3HT/Al.

The efficiency of polymeric devices is closely related to the material properties, *e.g.* morphology and surface topography.[28,29] This is particularly crucial for organic soft materials. The morphology depends on the polymer film thickness and coverage, thus influencing the charge transport properties, which are important for the performance and efficiency of the device.[10,30] An improved device rectification is therefore expected when SPAN is electropolymerized on the MITO substrate, resulting in a thicker SPAN layer covering the entire electrode substrate, which was confirmed with both SEM and AFM measurements. The fully covered and relatively ordered surface increases the effective interface area and is probably, together with the more regular surface morphology, responsible for the improved rectification response when using MITO. Thus, the addition of SPAN as hole transport layer in the MITO/SPAN/RR-P3HT/Al configuration improved positive charge injection in the device.

4 Conclusions

A new method for electropolymerization of SPAN with good surface coverage and a sulfonation degree of approximately 30% is presented. The method is based on surface modification of ITO with aniline silane (MITO), which results in a highly improved rectification response (I–V characteristics) of MITO/SPAN/RR-P3HT/Al devices compared with similar devices prepared on unmodified ITO substrates. The positive charge injection is effectively improved by the surface modification, which is reflected in the increase of the rectification value from *ca.* 1×10^2 (unmodified ITO) to 1×10^4 (MITO). It is shown that the SPAN film covers the entire MITO substrate unlike films grown on unmodified ITO. This is probably the main reason for the improved rectification response of these devices.

In order to prepare the MITO/SPAN/RR-P3HT/Al devices with good reproducibility, it is important to control the oxidation state of the SPAN film and convert it to the electrically conducting ES form prior to the spin-coating of the RR-P3HT top layer. This can be achieved by appropriate post-treatment of the film at a sufficiently high positive potential after the electropolymerization in combination with acid washing. The method is simple and ensures precise control of the oxidation state of the SPAN layer.

The MITO/SPAN/RR-P3HT/Al devices may find possible application areas within organic photovoltaics. Among many possible applications, the highly improved rectification response may turn out to be a useful property in organic electronics.

5 Experimental

5.1 Chemicals

3-Aminobenzenesulfonic acid (3-ABA; metanilic acid) (≥98.0%), aniline (≥99.5%) and [3-(phenylamino)propyl]trimethoxysilane (aniline silane) (≥95%) were obtained from Fluka. Methanol (≥99.8%), perchloric acid and sulfuric acid were from J. T. Baker, and hydrogen peroxide from Aldrich. Regio-regular poly(3-hexylthiophene) (RR-P3HT) (HT linkage >96%, MW 36 500) was obtained from Merck Chemicals, and trichloromethane (chloroform) from Riedel-deHaën. Ultra pure deionized water (ELGA, $R \geq 18.2$ MΩ) was used in all experiments. All chemicals were used as received and all solutions were purged with nitrogen prior to use.

5.2 Surface modification of ITO

The ITO glasses (Planar International; thickness: 1 mm) were cut to 3 cm × 1 cm slides, and then cleaned by ultrasonication in separate solutions of acetone, ethanol, and water for 10 min each. Both sides of the glass pieces were further cleaned in a plasma cleaner (Harrick, PDC-001) for 10 min. The cleaned ITO glasses were then conditioned for 5 h in a piranha solution mixture of concentrated sulfuric acid and hydrogen peroxide (volume ratio: 7 : 3) in order to produce more hydroxy groups on the ITO surface.[12] After the piranha treatment, the ITO glasses were washed with copious amounts of water and dried under nitrogen gas. These pre-treated substrates were surface modified by placing them for 24 h in a methanol solution containing 10 mM aniline silane (Scheme 2).[12] The ITO substrates modified with aniline silane (MITO) were then washed thoroughly with methanol and dried under nitrogen

gas at room temperature before the electropolymerization was started. A simplified chemical structure of SPAN is shown in Scheme 2 with a sulfonation degree of 50%.

5.3 Electropolymerization

The SPAN films were electropolymerized by cyclic voltammetry (CV) in an aqueous solution containing 0.1 M 3-ABA, 0.01 M aniline and 0.4 M $HClO_4$. The MITO glass, a Pt wire and a Ag|AgCl wire was used as the working, counter and reference electrode, respectively. The potential was cycled between −0.3 V and 0.8 V at a scan rate of 50 mV s^{-1} for 50 cycles and the potential was controlled with an Autolab (PGSTAT 20) potentiostat. Prior to all measurements the solutions were purged with nitrogen and the solutions were blanketed with nitrogen during the experiments. After the electropolymerization, the SPAN films were polarized at 0.3 V (*vs.* Ag/AgCl) for 10 min and thereafter washed with 0.4 M $HClO_4$. This is essential in order to keep the films in the electrically conducting ES form and to avoid conversion to the non-conducting EB form prior to the spin-coating of the RR-P3HT layer on top of the SPAN layer (Scheme 2).

5.4 Scanning electron microscopy (SEM) and atomic force microscopy (AFM)

The morphologies of the SPAN films electropolymerized on ITO and MITO were studied and compared by SEM and AFM. The SEM micrographs were obtained with a Leica Cambridge Instruments Stereoscan 360 instrument. The thickness of the SPAN films was measured in non-contact mode with an AFM Autoprobe CP instrument (Parc Scientific Instruments). All AFM measurements were performed in the presence of air.

5.5 X-Ray photoelectron spectroscopy (XPS)

A Perkin-Elmer 5400 ESCA instrument was used in the XPS measurements with monochromatized Al Kα radiation (1486.6 eV) and a pass energy value of 17.9 eV. In order to obtain a sufficient rate of photoelectron pulses, the pass energy was increased to 44.75 eV for the SPAN films that were polarized at 0.3 V for 10 min and rinsed with 0.4 M $HClO_4$. For this reason, the XPS signal is slightly wider in Fig. 4b than in Fig. 4a. Sensitivity factors used in determining atomic concentration ratios were 0.296, 0.477, and 0.570 for C 1s, N 1s, and S 2p, respectively. The C 1s line at 284.7 eV was used as the binding energy reference. All samples were in contact with air prior to the XPS analysis and the pressure in the vacuum chamber was 2×10^{-9} mbar during the measurements. The quantitative accuracy of the atomic concentrations determined by XPS is usually within 10–20% because photoionization cross-sections may depend on the chemical environment of the studied element. However, a better precision can be obtained for the different SPAN films since they resemble each other.

5.6 Fourier transform infrared spectroscopy (FTIR)

The FTIR measurements were performed with a Bruker IFS 66/S spectrometer equipped with a seagull™ variable angle reflectance accessory (Harrick Scientific). An MCT detector was cooled with liquid nitrogen. The incidence angle was set to 80° and 2000 interferograms were recorded with a resolution of 4 cm^{-1} for each spectrum. The sample holder was purged with N_2. The spectra of the SPAN films were background corrected with the spectra of either bare MITO or ITO.

5.7 UV-VIS spectroscopy

The pH sensitivity of the SPAN films was studied with UV-VIS measurements. Background spectra were always recorded with two blank MITO glasses (without SPAN films). The UV-VIS transmission spectra were measured between pH 2 and 12 with a Hitachi U-2001 spectrophotometer. Separate pH buffer solutions for each pH consisting of 25 mM of citric acid, Tris, KCl, KH_2PO_4 and $Na_2B_4O_7$ were prepared with deionized water ($R \geqslant 18.2$ MΩ) according to Perrin and Dempsey.[31] The UV-VIS spectrum of the SPAN film prepared on the MITO glass was measured in each buffer solution after an equilibration time of 30 min.

5.8 Current–voltage measurements

10 mg ml^{-1} RR-P3HT was dissolved in water-free chloroform and the solution was filtered through a 0.2 μm size filter before the RR-P3HT film (thickness: 150 nm) was spin-coated (1000 rpm) on top of the SPAN layer. The RR-P3HT film preparation procedure was carried out in a controlled N_2 atmosphere to avoid contamination by oxygen and water. Finally, 50 nm thick aluminium top contacts (2–10 mm^2) were evaporated on top of the RR-P3HT film under vacuum ($<10^{-6}$ mbar). Current–voltage measurements were performed with a Keithley 2400 SourceMeter and the samples were kept under vacuum during the measurements. A delay time of a few seconds, which was much longer than the RC decay time constant, was used to ensure full voltage drop over the samples.

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