

Polypyrrole self-organized nanopore arrays formed by controlled electropolymerization in TiO₂ nanotube template

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ESI1. Electropolymerization reactions.

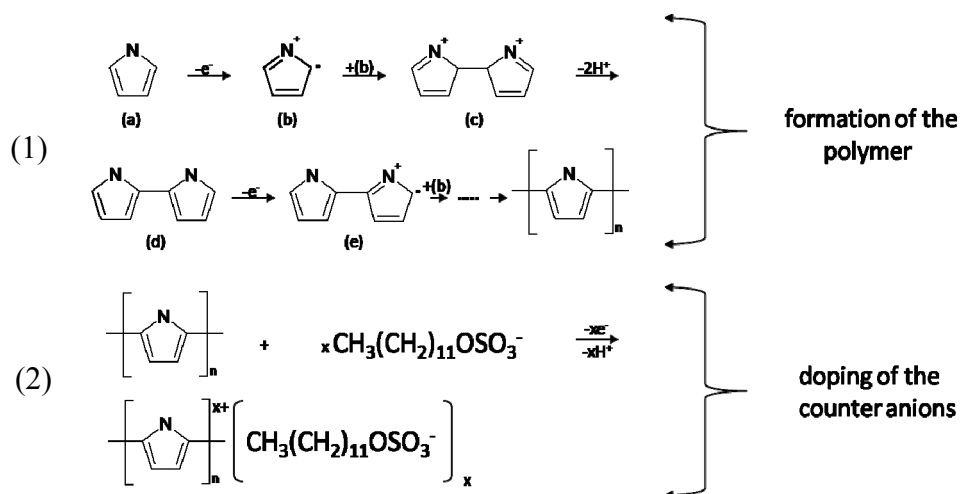


Fig. ESI1 Reactions of anodic oxidation of pyrrole (1) oxidation pyrrole monomer, (2) doping of dodecylsulfate counter-ions.

ESI2. Pulse current protocol

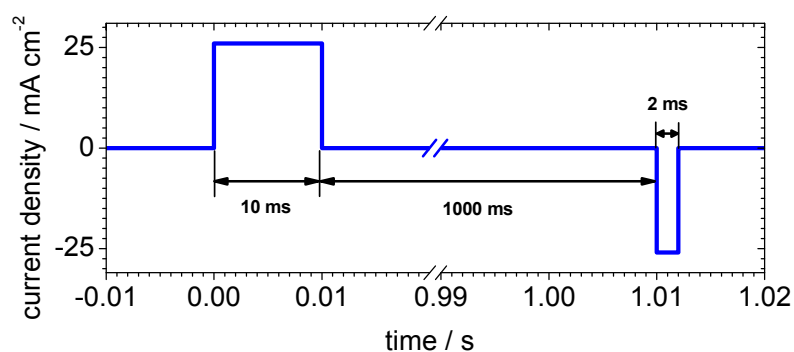


Fig. ESI2 Pulse current protocol used for electropolymerization of pyrrole into TiO₂ matrix.

ESI3. Chemical structure of polypyrrole nanopore arrays

XPS surface analysis

The C 1s, O1s, N1s and S2p core level spectra shown in Figs ESI3 and 2b are typical for doped polypyrrole. The C1s is centered at about 284.8 eV. The carbon peak is asymmetric and can be decomposed into three lines by shape analysis with Gaussian-Lorentzian fitting functions (Fig. ESI3a). The line at lowest binding energy is located at 284.3 with a linewidth of 1.4 eV, whereas the second peak at 285.1 eV has a linewidth of 1.4 eV. These lines are typically recognized as α and β carbons in the polypyrrole ring, respectively.^{1,2} The energy splitting between the peaks is 0.8 eV and is slightly lower than that of α and β carbons in pyrrole monomer reported to be 0.9 eV.¹ It should be noted here that the shape of the lines may be affected by the presence of doped aliphatic hydrocarbons. The third Gaussian-Lorentzian component is located at 286.3 and has much larger linewidth of 2.81 eV and may be associated with the presence of doped hydrocarbons and contaminants. The relative contributions of the three peaks are 0.32, 0.37 and 0.31. Due to the presence of organic dopant the photoemission peaks can not be unambiguously further resolved in the C 1s core level spectrum.

The O 1s core level peak is as expected located at 532.2 eV. Similarly to C 1s, the N 1s core level shows an asymmetry on the high binding energy side. Deconvolution of N 1s region clearly indicates presence of two nitrogen heteroatoms. The main N peak located at 400.0 eV with a linewidth 1.5 eV is attributed to neutral N in the neutral pyrrole ring. The second peak with a linewidth of 2.9 eV is located at 401.3 eV. The shift of 1.3 eV to the higher binding energy is attributed to the electrostatic interaction with doped anions. The deconvolution analysis of N 1s region shows contributions of neutral and charged nitrogen atoms with atomic ratio of 0.31, which simply means that *c.a.* 31% of the pyrrole rings in polypyrrole chain are involved in electrostatic interaction with doped anions. The S 2p region clearly indicates that the dodecylsulphate anions are incorporated into polypyrrole nanopore arrays. The core level peak is located at *c.a.* 168.7 eV (inset in Fig.2b) with atomic S:N ratio of 0.27. The calculated doping level of counter-ions from S:N ratio is slightly lower than the number of pyrrole rings involved in electrostatic interaction. The atomic ratio of C:N is 7.8 and assuming 4C in pyrrole ring, 12C in doped counter-anion, gives doping ratio of 0.32. The values of doping level are of approximately equal magnitude and are in line with the doping level in bulk polypyrrole obtained by EDX analysis (see Tab.1).

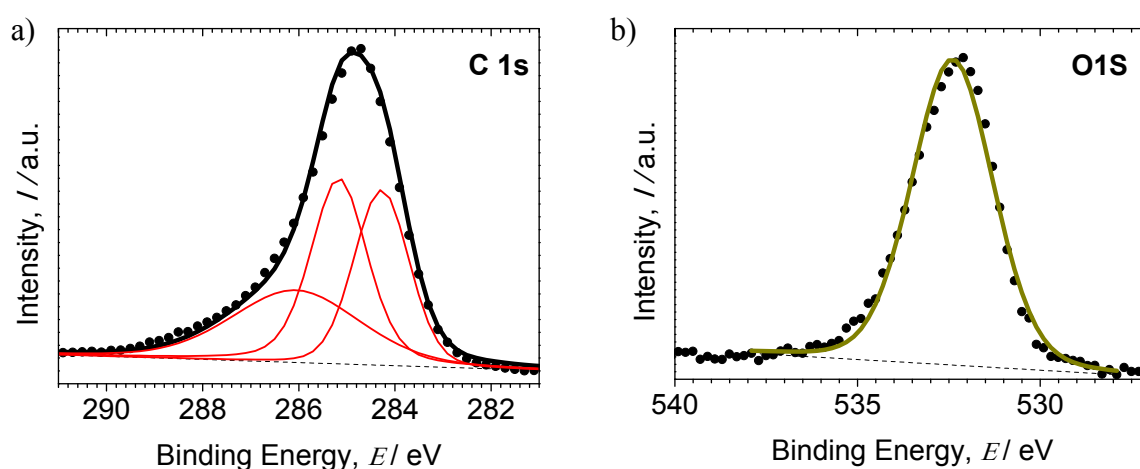


Fig. ESI3 Core level photoelectron peaks for polypyrrole nanopore arrays formed in TiO₂ nanotubes grown by anodization at 30V, a) C 1s b) O 1s.

Tab 1 .Stoichiometry of polypyrrole nanopore arrays formed in TiO₂ nanotubes grown by anodization at 30V.

Method	Type of calculation	Doping level or oxidation state, x	Number of pyrrole rings per one doped counter-ion, 1/x
XPS	-N ⁻ : -N ⁺	0.31*	3.2
	C:N	0.32**	3.1
	S:N	0.27**	3.7
EDX	C:N	0.33**	3.0
	S:N	0.34**	2.9

* oxidation state of polypyrrole,

** doping level

ToF-SIMS surface analysis

The negative secondary ion ToF-SIMS spectra in the range 0-300 mass unit are shown in Fig. ESI4. The peaks in the range 0-25 (H⁻, C⁻, CH⁻, N⁻, O⁻, OH⁻, C₂⁻, C₂H⁻) can be assigned to low mass fragments of polypyrrole and dopant, and/or surface contaminations. The peak at m/z 19 is assigned to F⁻ ions, which means that some amount of fluoride ions is adsorbed on the surface or/and is partially incorporated into polypyrrole nanopore arrays. The peak at m/z 26 is the most indicative peak assigned to CN⁻ ion characteristic for polypyrroles. The peaks at m/z 80 (SO₃⁻), 96 (SO₄⁻), 97 (HSO₄⁻) and 256 (C₁₂H₂₅OSO₃⁻) are characteristic for the dodecylsulphate ion and indicate that polypyrrole is doped with these ions. The negative ion spectra clearly identify chemical nature of two different components in conducting polymer nanopore array matrix *i.e.* polypyrrole and the dodecylsulphate counter-ion.

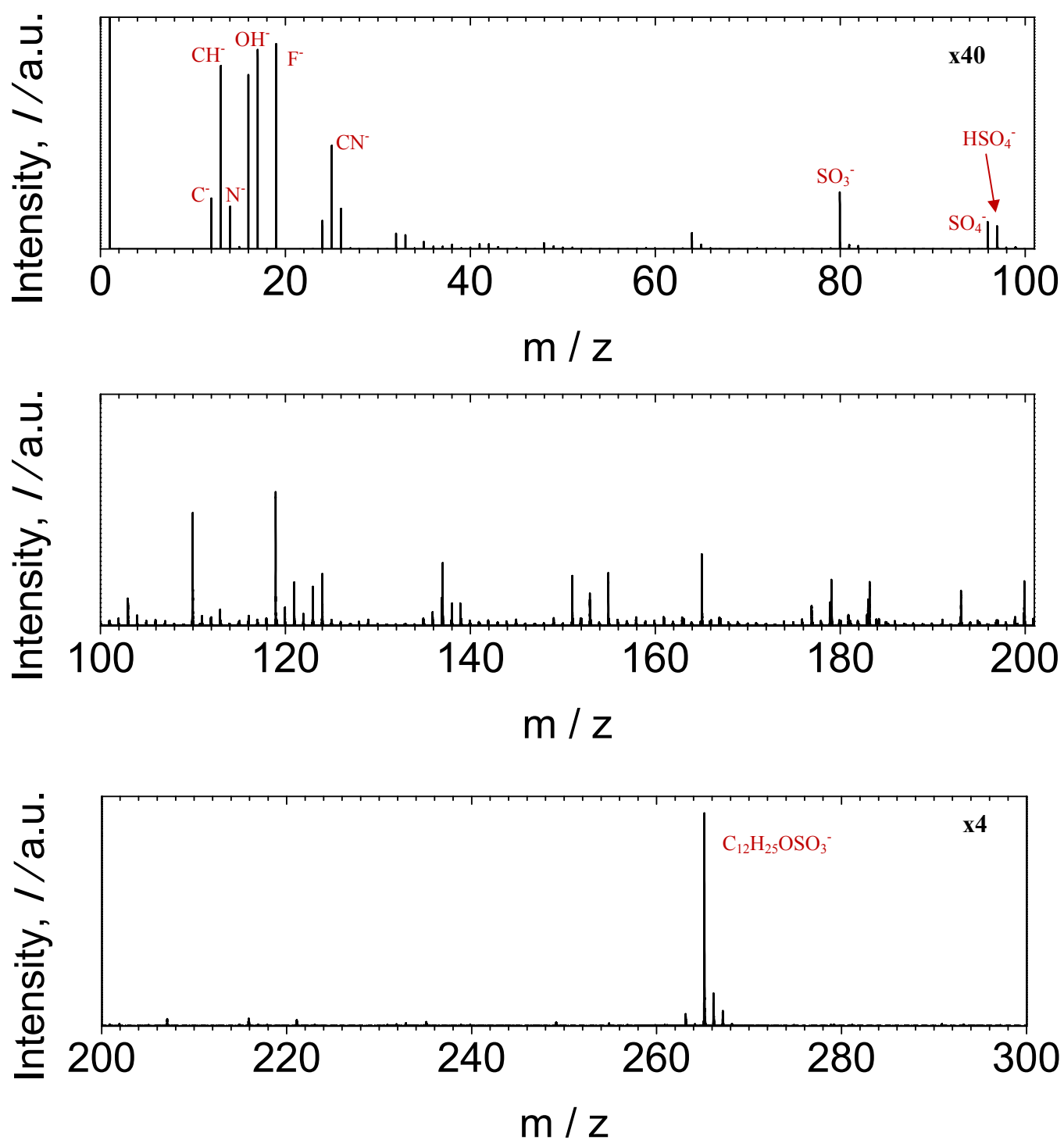


Fig. ESI4 Negative ion ToF-SIMS spectra obtained for polypyrrole nanopore arrays formed in TiO_2 nanotubes grown by anodization at 30V.

