Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2010

Conducting polymer

ELECTRONIC SUPLEMENTARY INFORMATION

Polypyrrole self-organized nanopore arrays formed by controlled electropolymerization in TiO_2 nanotube template

Damian Kowalski* and Patrik Schmuki*
Department of Materials Science, University of Erlangen-Nurnberg,
Martensstrasse 7,D-91058 Erlangen,Germany. Fax:+49-9131-85 275 82; Tel:+49-9131-85 275 82;
E-mail: kowalski@cat.hokudai.ac.jp , E-mail: patrik.schmuki@ww.uni-erlangen.de

ESI1. Electropolymerization reactions.

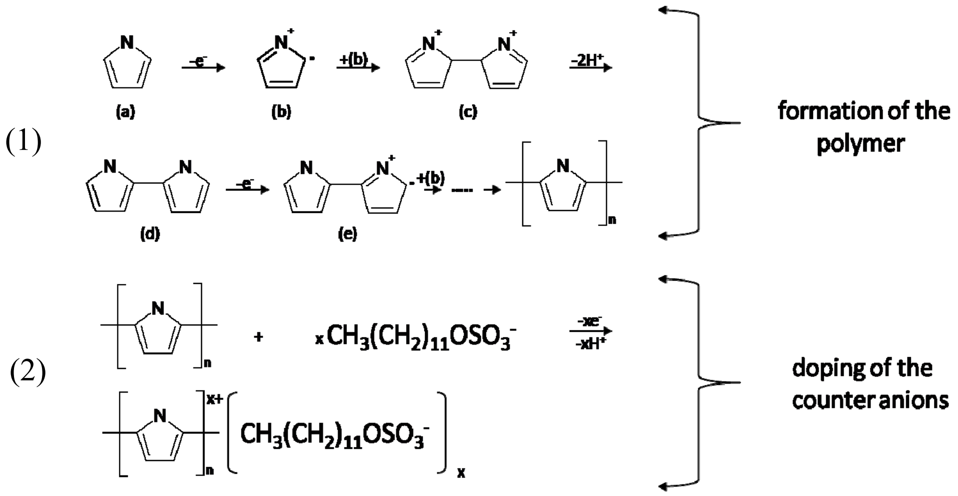

Fig. ESI1 Reactions of anidic oxidation of pyrrole (1) oxidation pyrrole monomer, (2) doping of dodecylsulfate counter-ions.

ESI2. Pulse current protocol

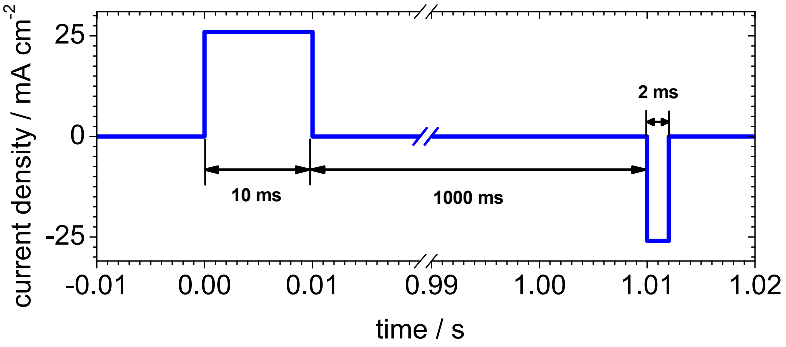

Fig. ESI2 Pulse current protocol used for electropolymerization of pyrrole into TiO_2 matrix.

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-Lorenzian fitting functions (Fig. ESI3a). The line at lowest binding energy is located at 284.3 with a linewidh of 1.4 eV, whreas the second peak at 285.1 eV has a linewidh 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-Lorenzian component is located at 286.3 and has much larger linewith 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 linewidh 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).

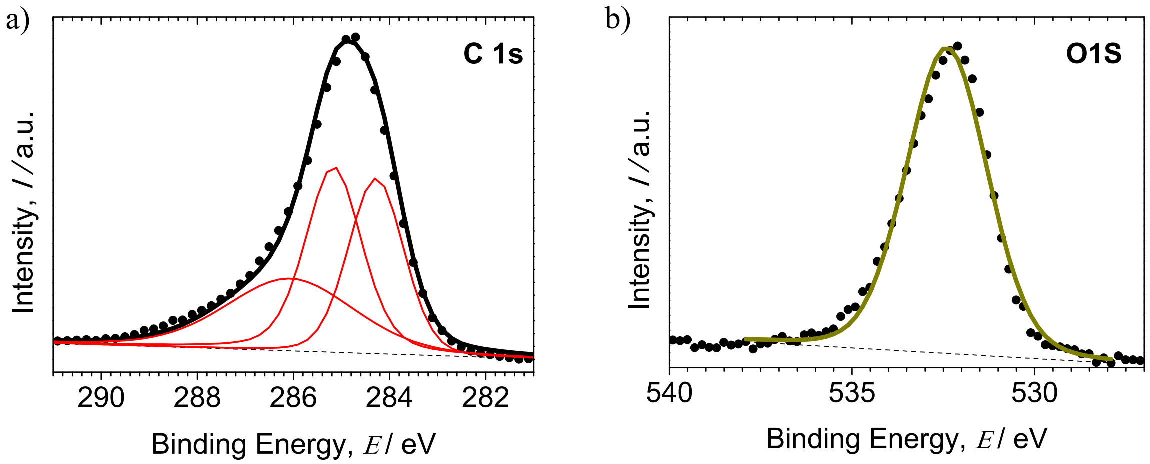

Fig. ESI3 Core level photoelectron peaks for polypyrrole nanopore arrays formed in TiO_2 nanotubes grown by anodization at 30V, a) C 1s b) O 1s.

Tab 1 .Stoichiometry of polypyrrole nanopore arrays formed in TiO_2 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^-, C_2^-, C_2H^-) 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 (SO_3^-), 96 (SO_4^-), 97 (HSO_4^-) and 256 ($C_{12}H_{25}OSO_3^-$) 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.

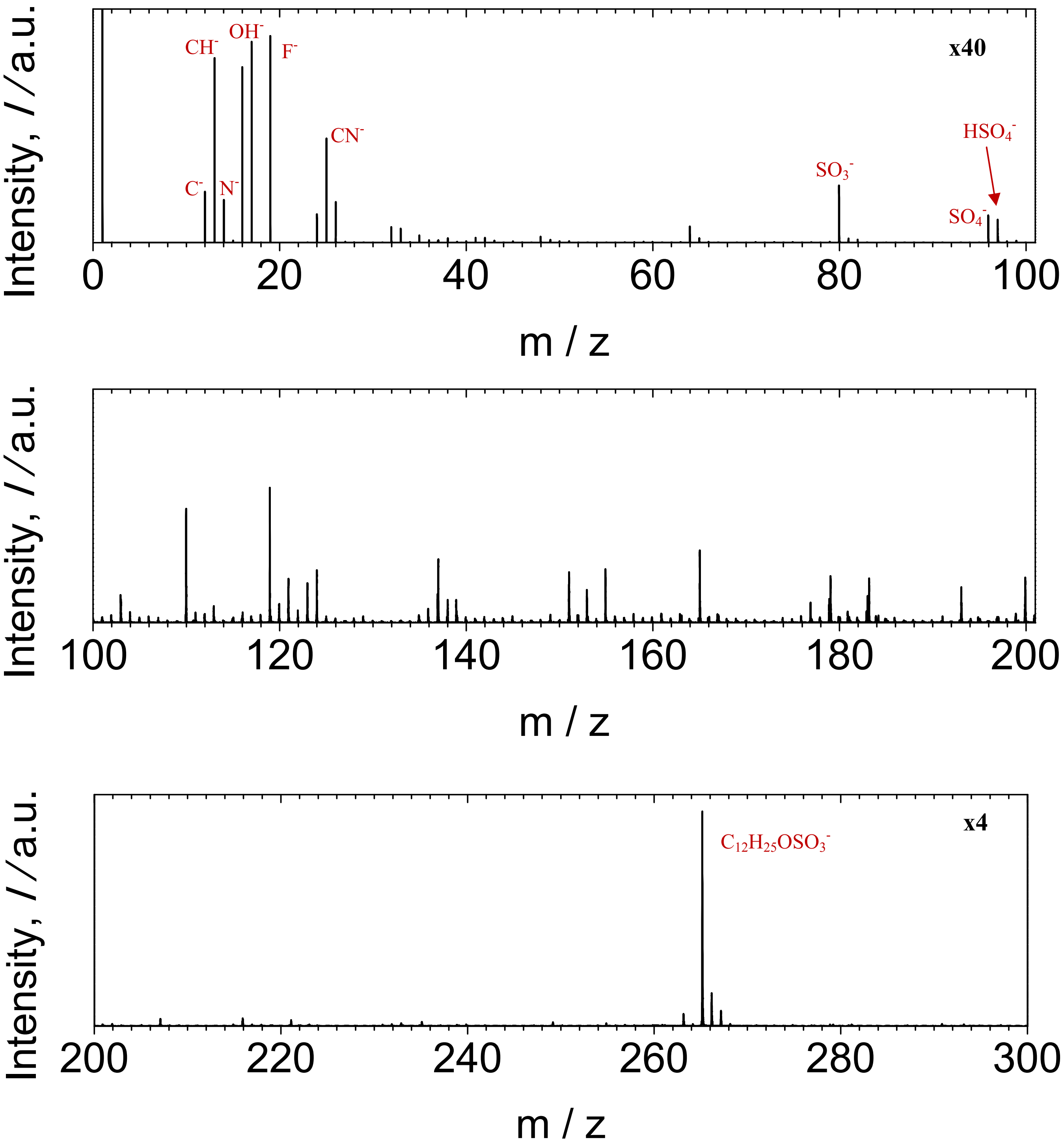

Fig. ESI4 Negative ion ToF-SIMS spectra obtained for polypyrrole nanopore arrays formed in TiO_2 nanotubes grown by anodization at 30V.

ESI4. Electrochemistry of polypyrrole nanopore arrays.

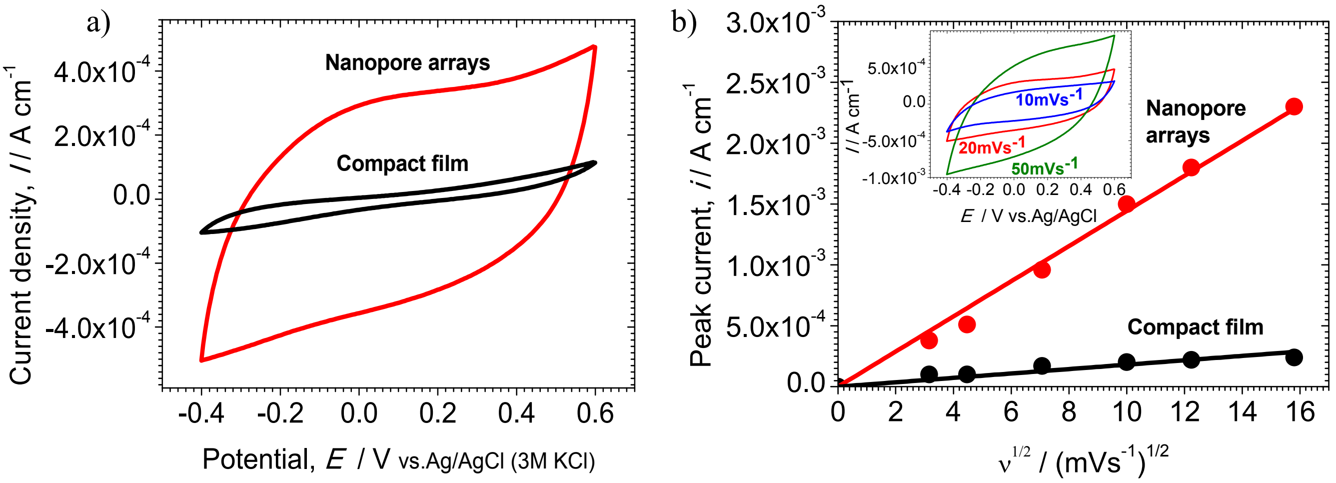

Fig. ESI5 Cyclic voltammetry (CV) studies of polypyrrole in 1M $LiClO_4$ - propylene carbonate electrolyte; a) CVs, b) peak current as a function of square root of sweep potential rate.

The electrochemical behaviour of the polypyrrole nanopore arrays formed in TiO_2 nanotubes grown by anodization at 30V is demonstrated by cyclic voltammetry (CV) in 1M $LiClO_4$ - propylene carbonate electrolyte. Figure ESI5 shows 10th consecutive cycles performed in a nonaqueous Li^+ solution for compact polypyrrole film and nanopore arrays. More detailed mass transport studies for compact films by means of electrochemical quartz crystal microbalance (EQCM) showed that the major charge carriers are cations and consequently, anions are not involved in the mass transport process for polypyrrole electrodeposited from ionc-surfactant solution.[3] The present results clearly show reversibility of lithium ion insertion-release during reduction-oxidation process. The results (Fig. ESI5a) demonstrate that the nanopore arrays have much more enhancened capacity for Li^+ ions compared with the compact polymer films. The linear dependence of the peak current on square root of sweep potential rate, shown in Fig. ESI5b, indicates that the reaction is under diffusion control. The difference in slope of linear relationship clearly shows that the kinetics of lithium ion intercalation is affected by the morphology of polypyrrole.

ESI5. Polypyrrole deposited in TiO_2 nanotubes formed in ethylene glycol-water electrolyte

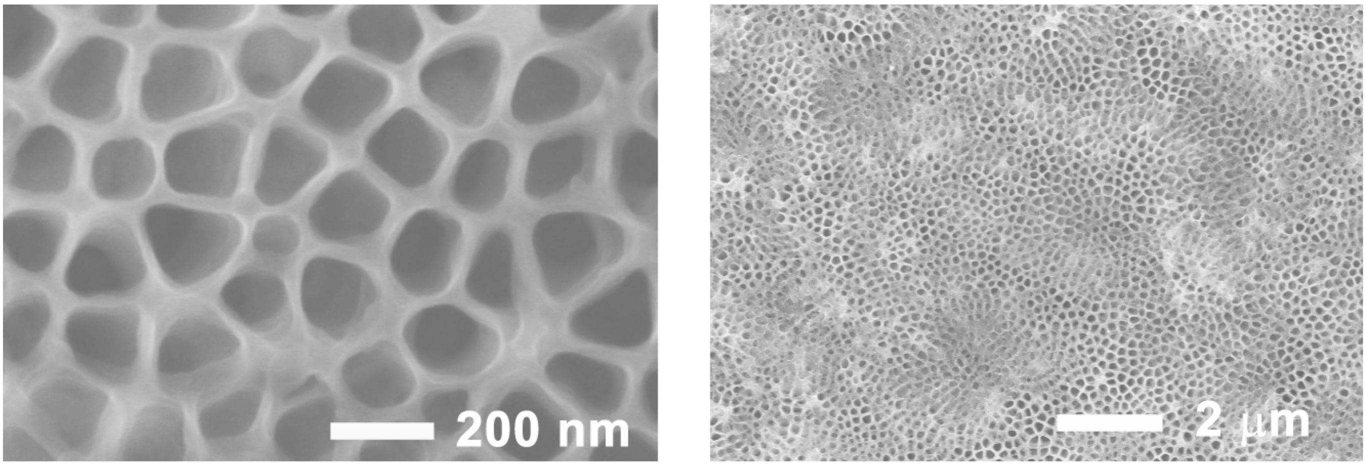

Fig. ESI6. Polypyrrole nanopore arrays fabricated by electropolymerization in TiO_2 nanotubes grown by anodization of Ti at 30V in ethylene glycol–water electrolyte (55:45 v/v) containing ammonium fluoride (0.1 M).

ESI6. Experimental Section

Titania nanotubes were formed by anodization of 0.1 mm thick titanium foils of purity 99.6 % purchased from Advent Materials. Before use, titanium specimens were degreased by sonication in acetone, isopropanol and methanol, rinsed in deionized Milli-Q water and dryed in a nitrogen stream. The foils were anodized in glycerol-water (55:45 v/v) electrolyte containing ammonium fluoride (0.27 M) at selected voltage from 10 to 30 V in line with the procedure described previously.[4] For comparison titania nanotubes were formed in ethylene glycol-water (55:45 v/v) electrolyte containing ammonium fluoride (0.1 M) at 30 V according to the procedure described elsewhere.[5] Anodization was carried out in a three-electrode cell (10 cm^3) with Ag/AgCl/3M KCl reference electrode with a Luggin capillary and platinum counter one. The geometrical surface of the titanium working electrode was 1 cm^2.

A three-electrode cell with 100 cm^3 volume was used for electropolymerization of pyrrole in TiO_2 nanotubes. A Ag/AgCl/3M KCl electrode with a Luggin capillary and a platinum foil were used as reference and counter electrodes, respectively. The geometrical area of working electrode (titania nanotubes) was 0.385 cm^2. The cell was under nitrogen atmosphere during all electrochemical experiments. The electropolymerization was carried out at room temperature in aqueous solution containing pyrrole monomer (0.1 M) and sodium dodecylsulfate (25 mM).[6] Pyrrole monomer purchased from Sigma-Aldrich (98% purity) was used without any pretreatment. Before polymerization, all solutions were deoxygenated by nitrogen bubbling for 30 min before use. The pulse current protocol with 10ms anodic pulse (+26 mA cm^{-2}), 1000 ms rest potential and 2ms cathodic pulse (-26 mA cm^{-2}) was applied for electropolymeryzation. After deposition step titania nanotubes were selectively dissolved in 5 vol.% hydrofluoric acid.

The samples for cyclic voltammetry (CV) were prepared as follows; Ti foil was anodized at 30V for 3 h, followed by pyrrole electoppolymeryzation in TiO_2 matrix for 6 min. Then c.a. 200nm thick gold layer was sputtered onto polypyrrole layer. After that the sample was transferred onto conducting cupper tape and treated with 5 vol.% HF for 20 min to dissolve TiO_2 template. The reference flat polypyrrole sample was prepared on flat Ti surface and transferred onto Cu tape in the same manner as the porous one. The CVs curves were recorded in 1M $LiClO_4$ - propylene carbonate electrolyte.

The anodizing and electropolymeryzation were carried out using JAISSLE IMP88PC-200V potentiostat/galvanostat coupled with PRODIS 1/161 and KEITHLEY 200 digital multimeter. The CVs were obtained using Autolab PGSTAT 302N.

The field emission scanning electron microscope (FE-SEM, Hitachi S4800) was used for structural and morphological characterization of titania nanotubes and nanostructured polymers. The composition of polymer was investigated by an energy dispersive X-ray analyser (EDAX) coupled to the FE-SEM. Surface analysis of polymer was carried out by X-ray photoelectron spectroscopy (XPS) PHI 5600 (Al Kα X-ray source). The energy calibration was carried out using Au $4f_{7/2}$ line of the gold substrate. The surface composition of doped polypyrrole was calculated from areas of C 1s, N 1s and S 2p photoelectron peaks corrected using the manufacturer provided sensitivity factors. The analysis of peaks included linear background subtraction and Gausian-Lorentzian line shape decomposition. Time-of-Flight SIMS measurements of polypyrrole nanopore arrays were performed on TOF.SIMS 5 spectrometer (ION-TOF, Munster). Secondary ion spectra were obtained in negative and positive static mode by using pulsed 25keV Bi_3^+ liquid metal ion beam. Spectra were recorded in high resolution mode ($m/\Delta m > 8000$ at ^{29}Si). The beam was electrochemically bunched down to 25 ns to increase the mass resolution and rastered over 500 x 500 μm^2 area. The positive spectra were less informative compared with the negative ones and are not reported here.

1. P. Pfluger and G. B. Street, *J Chem Phys*, 1984, **80**, 544-553.
2. L. Atanasoska, K. Naoi and W. H. Smyrl, *Chem Mater*, 1992, **4**, 988-994.
3. D. Kowalski, M. Ueda and T. Ohtsuka, *J.Mater.Chem.*, 2010.
4. J. M. Macak, H. Hildebrand, U. Marten-Jahns and P. Schmuki, *J Electroanal Chem*, 2008, **621**, 254-266.
5. S. Berger, J. Kunze, P. Schmuki, A. T. Valota, D. J. LeClere, P. Skeldon and G. E. Thompson, *J Electrochem Soc*, 2010, **157**, C18-C23.
6. D. Kowalski, M. Ueda and T. Ohtsuka, *Corros Sci*, 2007, **49**, 3442-3452.