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Direct chemical synthesis of pristine polypyrrole hydrogels and derived aerogels for high power density energy storage applications

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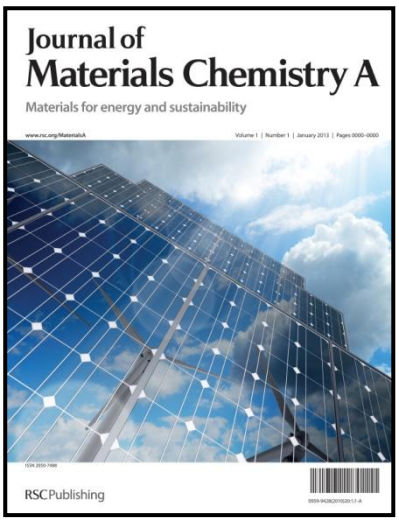
Complete List of Authors:	Temmer, Rauno; University of Tartu, IMS lab, Institute of Technology Kiefer, Rudolf; University of Tartu, IMS lab, Institute of Technology Aabloo, Alvo; University of Tartu, IMS lab, Institute of Technology Tamm, Tarmo; University of Tartu, IMS lab, Institute of Technology



Journal of Materials Chemistry A

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COMMUNICATION

Direct chemical synthesis of pristine polypyrrole hydrogels and derived aerogels for high power density energy storage applications

Rauno Temmer, Rudolf Kiefer, Alvo Aabloo and Tarmo Tamm*

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A direct chemical route for preparing pristine polypyrrole hydrogels and derived aerogels with specific surface area up to 425.8 m^2 g^{-1} is presented. The structure of the thick hydrogel electrodes relieves diffusion limitations of conventional polypyrrole-modified electrodes. Properties can be tuned by synthesis conditions and exchange of the dopant.

Polypyrrole (PPy) is perhaps the most available and extensively studied electronically conducting polymer (ECP) used for modifying the properties of other materials, may the target be implantable devices[1], sensing,[2,3] or energy storage.[2] The popularity of PPy can be related to its low environmental impact, ease of synthesis, durability, and virtually endlessly tuneable properties. Obtaining PPy-modified electrodes is possible electrochemically in form of compact film or performing chemical synthesis with some oxidizer and compacting the obtained powder or dispersion – the typical forms of chemically synthesized PPy.[4] In many application areas, particularly in energy storage, where despite the high theoretical specific energy storage capacity, the power density of ECP electrodes has been limited by the specific surface area, diffusion rate, and accessibility to ions, hence the attempts to introduce nano-structuring.[4,5] Typically, conductive gels have been made as composites where the structure is due to non-polymeric,[6] nonconductive polymer[7] networks (either pre-existing[8] or formed simultaneously with ECP polymerization[6]) or templates.[9] Another approach is to apply special derivates of common conductive polymers, enabling single-component gel formation,[10-12] using polyanionic dopants,[13,14] cross-linking agents[9,10,15] or multivalent metal cations[9,13,16] to form cross-linked networks of conductive polymer chains. These approaches, however, introduce various restrictions for applicability, impairing one of the most important characteristics of ECPs – the possibility to tune properties for specific applications.

To our knowledge, the present work is the only single-step, low-cost method for chemical synthesis of pristine (unmodified, linker-free) PPy hydrogels, the very first report of pristine PPy aerogels, and a novel route to obtain PPy-derived carbon aerogels. In a narrow gap of synthesis conditions, mixing reagents, which are common for the synthesis of PPy nanostructures and composites in form of powders and dispersions: pyrrole (Py) monomer, ammonium peroxydisulfate (APS, $(NH_4)_2S_2O_8$) or disodium peroxydisulfate (SPS, $Na_2S_2O_8$) oxidant and sodium dodecylbenzenesulfonate (SDBS, $NaC_{18}H_{29}O_3S$) surfactant results in stable PPy hydrogels (see ESI Fig. S1a†). Polymerization proceeds under kinetic control, resulting in controllable contribution of dodecylbenzenesulfonate (DBS^-) and sulphate (SO_4^{2-}) doping anions, moreover, the gelation mechanism and structure of the hydrogel are controllable by reaction conditions. Although surfactant-supported while synthesized, the PPy hydrogel network allows redoping by redox cycling. Simplicity and small number of constraints of the method open a large variety of possibilities for modifications for various applications.

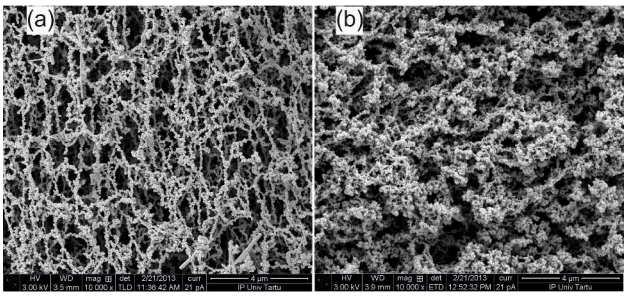

Fig 1 SEM micrographs (magnification 10,000×) of PPy aerogels. (a) 0.1 M Py-APS. (b) 0.3 M Py-APS.

Oxidizer solution was prepared separately from solution of Py and SDBS, the two were mixed together while stirring actively, followed by keeping still overnight (see ESI for experimental details†). To determine the reliable boundary conditions of the hydrogel synthesis, the concentrations of all components were varied. The key role is played by the surfactant concentration; optimal SDBS concentration for gel formation was found to be around 0.1 M with equal oxidizer and Py concentrations of 0.1–0.4 M. Lower SDBS concentrations resulted in very soft, fluid, difficult to handle hydrogels (still remaining intact in water), while higher concentrations resulted in water-soluble dispersions. Firmness of the gel was tuned by varying the concentrations of Py and APS (Py-APS) equally in range of 0.05–0.4 M. The gelation rate (Fig. S1c†) depended strongly on Py-APS concentration, taking from 10 s (0.4 M APS-Py) to 12 h (0.05 M APS-Py). Using SPS instead of APS had only minor influence on gel firmness. The proposed mechanism is that of micelle guided

growth[4] and cluster-to-cluster aggregation from surfactant solution at concentrations close to those of colloid formation.

Aerogels (Fig. 1a,b, ESI, Fig. S1b†) were prepared from the hydrogels by supercritical CO_2 extraction. The SEM micrograph of a gold sputter coated 0.1–0.2 M Py-APS aerogel (Fig. 1a, Fig. S2†) shows the structure to be a 3D-web of interconnected chains of small PPy nodules, while at higher concentrations (0.3–0.4 M Py-oxidant) coalescence was found to occur, with denser clusters and larger voids (Fig. 1b, for others concentrations, magnifications, and SPS oxidant see ESI, Fig. S2†).

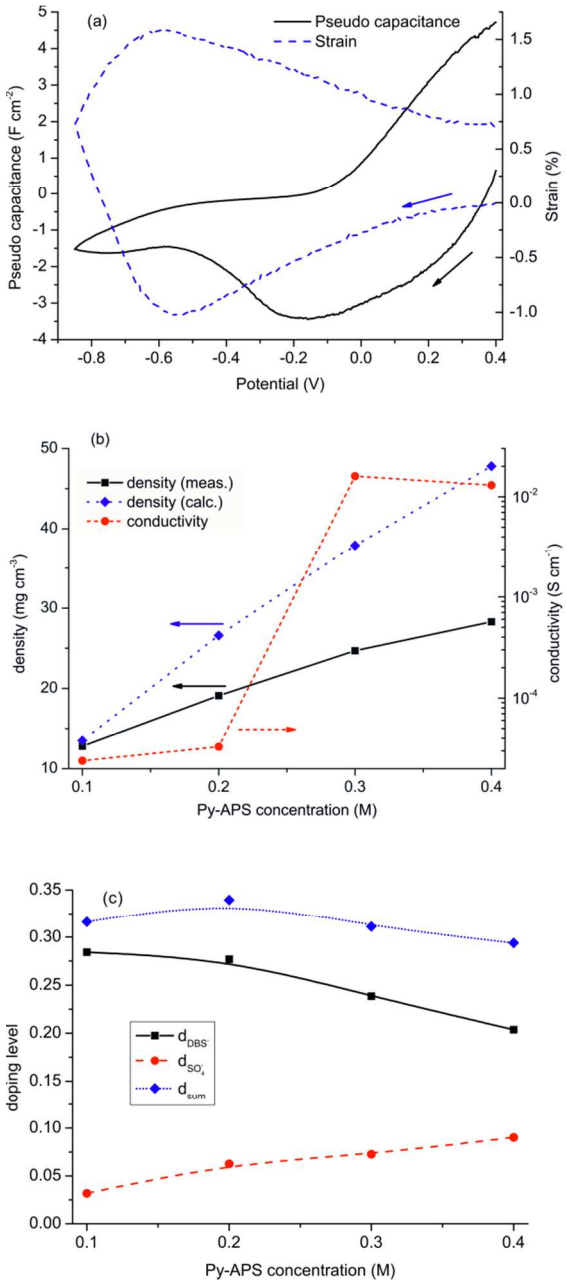

Fig. 2 (a) Electrochemical and ECMD measurements of the 0.3 M Py-APS hydrogel in 0.2 M $NaBF_4$ electrolyte. Pseudocapacitance and strain (scan rate 0.25 mV s^{-1}, surface area 18 cm^2). (b) Measured density (squares), calculated density (diamonds) and conductivity (circles), also ESI Table S3–S4). (c) Contributions of DBS^- (squares) and SO_4^{2-} (circles) anions to total doping of aerogels.

The qualitative difference in aerogels' morphology was characterized using cyclic voltammetry (CV) experiments on the respective hydrogels using fractal dimension (d_f) method (see ESI†).[17] d_f was found to be 1.7 and 2.1 for 0.2 M Py-APS and 0.3 M Py-APS hydrogels, respectively. According to computer simulations,[18] d_f = 1.7 is characteristic of diffusion limited cluster-cluster aggregation; the transition to reaction limited cluster-cluster aggregation (d_f = 2.2–2.3) kinetics is related to gelation speed,[18] which was found to increase with increasing Py-APS concentration.

Electrochemical properties of the 0.3 M Py-APS hydrogel were assessed using CV experiments and electrochemical impedance spectroscopy (EIS) in 0.2 M $NaBF_4$ electrolyte. The mobility of ionic species was studied using electro-chemo-mechanical deformation (ECMD) technique, which showed mixed ion mobility (see Fig. 2a and ESI†). The specific capacitance was measured to be respectable (considering electrode bulk) 159.1 F g^{-1}, with charge storage capacity of 198.8 C g^{-1}.

The results of the EIS (see ESI, Fig. S4†) indicate cylindrical diffusion with finite reflective boundaries, characteristic of thin films, dominating at low frequencies. The series resistance (R_E) value between the electrolyte and electrode was found to be 5.4 Ω.

The measured densities (12.8–28.3 mg cm^{-3}) of the aerogels depending on reactant concentrations (0.1–0.4 M Py-APS, respectively) were somewhat lower than expected (13.5–47.8 mg cm^{-3}, see Fig. 2b, Table S3†).

The conductivities of the aerogels show a clear demarcation depending on the reactant concentration (Fig. 2b, Table S3†), with those of denser gels close to the values reported by DeArmitt *et al.*[4] (*ca.* 0.01 S cm^{-1}) for PPy/DBS compressed pellets and cast films. This demarcation can be explained by the aforementioned qualitative structural differences between the sparse web of 0.1–0.2 M and 0.3–0.4 M Py-APS hydrogels, where increased contact area was found to improve percolation through PPy clusters. The slightly lower conductivity of 0.4 M Py-APS as compared to 0.3 M Py-APS can be explained by higher synthesis temperature (*ca.* 60 °C), causing more PPy conjugation defects. Similarly, optimum at Py:SDBS molar ratio 2.5 has been found by Wen *et al.* for PPy/DBS conductivity.[19]

Elemental analysis by energy dispersive X-ray spectrometry allowed separation of doping contributions from APS (SO_4^{2-}) and SDBS (DBS^-) (see Fig. 2c, Table S4†). While the overall doping level remained roughly constant, the contributions qualitatively followed the APS:SDBS ratio, indicating kinetic control of the polymerization process. The increasing discord between the measured and calculated densities and the slightly lower total doping levels with increasing Py-APS concentrations and APS:SDBS ratios (see Table S3†) was attributed to the less complete polymerization in denser hydrogels and higher solubility of DBS^--doped oligomers[19] in acetone used for the preparation of aerogels (solvent obtains transparent dark blue colour which was reversibly switchable by acid and base treatment). This discrepancy expresses polymerization efficiency, which was lower for denser hydrogels.

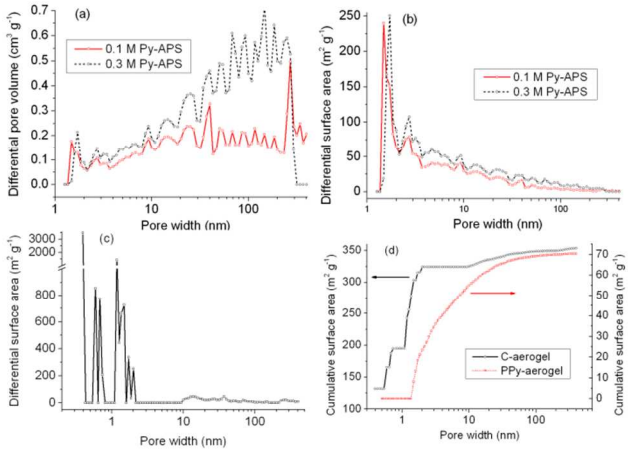

Fig. 3 N_2 sorption measurements of PPy and carbon aerogels. (a) Differential pore volume (0.1 and 0.3 M Py-APS). (b) Differential surface area (0.1 and 0.3 M Py-APS). (c) Differential surface area (0.1 M Py-APS derived carbon aerogel). (d) Cumulative surface area PPy (squares) and carbon (circles) aerogels (0.1 M Py-APS).

Specific surface area was characterized using the Brunauer-Emmett-Teller (BET) method and the qualitative pore size distribution of the aerogels (Fig. 3) using the DFT method. The measurements showed that 0.3 M Py-APS concentration yielded somewhat higher BET specific surface area (167.1 m^2 g^{-1}) compared to that of 0.1 M (134.4 m^2 g^{-1}). The higher concentrations also yielded almost double specific total volume of pores (0.73 *vs.* 0.39 cm^3 g^{-1}), while the specific micropore volume (2.7×10^{-3} *vs.* 7.4×10^{-3} cm^3 g^{-1}) for pore size $p < 300$ nm was smaller than that of the lower concentrations. The most significant qualitative difference was the peak (Fig. 3a,b) at pore width in range of 1–2 nm, which is assumed to reflect the difference in PPy inter-chain distances induced by dopant.

Activated PPy-derived carbon powder with high surface area can be prepared by carbonizing;[20] PPy aerogels can be carbonized as well, without loss of integrity and the continuous nature of the gel. The mass of the initial 0.1 M Py-APS aerogel was found to reduce by 29% upon carbonization at 350 °C for 12 h under vacuum, while the BET surface area was found to increase from 134.4 to 425.8 m^2 g^{-1} and the surface area *vs.* pore width graph (Fig. 3c,d) became similar to resorcinol-formaldehyde-derived carbon aerogels.[21]

In order to elucidate the feasibility of further functionalization *e.g.* for (ion) sensing applications, redoping experiments were carried out using CV for 0.3 M Py-APS hydrogels in 0.2 M $NaBF_4$ and $LiClO_4$ electrolytes (50 cycles, E = 0.4 ... -0.85 V, scan rate 0.25 mV s^{-1}). Elemental analysis showed that due to the stronger binding of double-charged SO_4^{2-} anions[22] and despite the larger size, mostly DBS^- anions were exchanged (see ESI, Table S5-S7†).

During long term (several months) continuous CV experiments, the hydrogel electrodes remained visually and electrochemically unaltered while sustaining exchange of DBS^- dopant anions for BF_4^- and for ClO_4^-. The hydrogel electrodes retained their total electrochemical doping level (becoming more anion-exchanging) and physical structure, while the CV performance was governed by the diffusion rate of the dominant mobile ion and the scan rate used. The stable behaviour upon redoping in different electrolytes indicates that the surfactant anion is not the binding component in the hydrogel. Additionally, the synthesis of 0.3 M Py-APS hydrogel in 1 M HCl solution was carried out, and despite reduced SO_4^{2-} contribution (Table S8†), stable hydrogel with identical appearance as before was obtained. Unlike polyaniline-poly(styrene sulfonate) hydrogels,[11] pristine PPy hydrogel did not decompose on long term electrochemical or chemical dedoping/deprotonation in 1 M NaOH solution, excluding the dominant role of the doping anions in the physical integrity (stability tested in pH range 1–14). Long term treatment with a variety of organic solvents also yielded no sign of decomposition.

Conclusions

To summarize, a very simple and straightforward method for obtaining pristine PPy hydrogels, leading to PPy and carbonized aerogels with tuneable internal physical structure and doping division is presented here. The method is based solely on well-known and extensively studied compounds. The lowest density obtained for PPy aerogel was 12.8 mg cm^{-3}, with highest specific BET surface area of 167.1 m^2 g^{-1} (for derived carbon aerogel 425.8 m^2 g^{-1}). The initial dopant anion could be exchanged to a large extent by redox cycling without hydrogel decomposition. While retaining the outstanding electrochemical properties of PPy, new exciting possibilities are opened up due to better accessibility to ions. Increased diffusion rate in bulk material improves applicability for high power density energy storage devices and high sensitivity sensors. Moreover, PPy hydrogels could be used as a scaffold for further refining and functionalization through electrochemical modification. Due to the large surface area (compared to the area of the electrical contact) and the continuous nature of the hydrogel, it is more appropriate to address them as hydrogel electrodes, rather than modifications to some underlying electrode material.

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Notes and references

Intelligent Materials and Systems Lab, Institute of Technology, University of Tartu, Nooruse 1, Tartu, 50411, Estonia. E-mail: tarmo.tamm@ut.ee

† Electronic Supplementary Information (ESI) available: experimental details, SEM micrographs, relevant numerical data and supporting argumentation. See DOI: 10.1039/b000000x/

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Electronic Supplementary Information

Direct chemical synthesis of pristine polypyrrole hydrogels and derived aerogels for high power density energy storage applications

Rauno Temmer, Rudolf Kiefer, Alvo Aabloo and Tarmo Tamm*

Intelligent Materials and Systems Lab, Institute of Technology, University of Tartu, Nooruse 1, Tartu, 50411, Estonia. E-mail: tarmo.tamm@ut.ee

Experimental details

Materials. Pyrrole (Py, Sigma-Aldrich) was distilled at reduced pressure and stored under argon atmosphere at low temperature in the dark. Ammonium peroxydisulfate (APS, $(NH_4)_2S_2O_8$, ≥ 98.0%, Sigma-Aldrich), sodium peroxydisulfate (SPS, $Na_2S_2O_8$, AG Chemia), sodium dodecylbenzenesulfonate (SDBS, $NaC_{18}H_{29}O_3S$, Sigma-Aldrich), sodium hydroxide (NaOH, ≥ 98.0%, Lach-Ner s.r.o., Czech Republic) and lithium perchlorate ($LiClO_4$, ≥ 98.0%, Fluka) were used as received. Sodium tetrafluoroborate ($NaBF_4$, Reahim) was additionally purified by recrystallization. Ultra pure MilliQ+ water and HPLC grade propanone (acetone, Ac, Rathburn Chemicals Ltd) were used. All synthesis solutions were degassed in ultrasonic bath and saturated with Ar.

Hydrogel synthesis. (Fig. S1a) Py monomer with SDBS surfactant and oxidant (APS or SPS), respectively, were dissolved in two beakers, in equal volumes of solvent (water or 1 M HCl solution). Optimal SDBS concentration for gel formation was found to be around 0.1 M (all concentrations given in respect to the final volume of hydrogel) with equal oxidizer and Py concentrations of 0.05–0.4 M (oxidizer:Py molar ratio 1:1). All hydrogels (see Table S1) were polymerized from separately prepared solutions. Both solutions were then poured together while stirring until solution turned dark grey (approximately 3–10 s). The solution was then immediately poured into glass mould and kept still overnight to complete gelation. Polymerization was monitored using pH-meter DVM8681 (Velleman) and successful formation of the hydrogel was confirmed by tilting in air or in liquid (softer samples) and further by testing its stability against decomposition in water during washing. After gelation, hydrogels were carefully removed from the mould and washed for 1 week by immersion in water (replaced every 12 h) to remove any unreacted Py, detached Py oligomers and remains of SDBS and oxidant.

Table S1. Prepared hydrogel samples (all concentrations given in respect to the final volume of hydrogel).

Sample designation	SDBS concentration (M)	Py concentration (M)	Oxidant and concentration (M)	Result description
-	0.1	0.05	APS, 0.05	Soft gel
0.1 M Py-APS	0.1	0.1	APS, 0.1	Normal gelation
0.2 M Py-APS	0.1	0.2	APS, 0.2	Normal gelation
0.3 M Py-APS	0.1	0.3	APS, 0.3	Firm gel instantly
0.4 M Py-APS	0.1	0.4	APS, 0.4	Slightly crumbling firm gel instantly
-	0.2	0.2	APS, 0.2	No gelation
-	0.05	0.1	APS, 0.1	Very soft, almost liquid gel
-	0.1	0.3	SPS, 0.3	Normal gelation
-	0.1	0.3	APS, 0.3	More elastic gel instantly*

* polymerized in 1.0 M HCl solution

Aerogel preparation. (Fig. S1b) The solvent was exchanged from water to Ac by immersing the hydrogel in a beaker containing Ac. The hydrogel was placed on a stainless steel mesh that allowed the higher density water to collect at the bottom of the beaker. The hydrogel was washed (5–7 solvent exchanges) until the washing Ac remained pale, rather than dark blue. The dark blue washing residue was collected and dried in N_2 atmosphere for elemental analysis. After solvent exchange, hydrogels were dried using continuous supercritical CO_2 extraction, similar to the procedure described elsewhere[1]; detailed description of the optimized procedure is available upon request from Tarmo Tamm, tarmo.tamm@ut.ee.

Characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). For SEM imaging aerogel samples were sputter-coated with gold and images were taken using Helios NanoLab 600 SEM. Elemental composition was determined using EDX (Hitachi TM3000 with SwiftED 3000).

Electrochemical and electro-chemo-mechanical deformation (ECMD) measurements.

Electrochemical and ECMD characterization was performed for 0.3 M Py-APS concentration hydrogel in 0.2 M $NaBF_4$ (also in 0.2 M $LiClO_4$ for redoping experiments) solution using potentiostat/galvanostat PARSTAT 2273. Measurements were performed in a one-compartment three-electrode cell. The hydrogel was gelated in cylindrical cup (48 mm diameter, top surface area 18 cm^2, hydrogel volume 15 cm^3) on top of a sparse platinum wire (Ø 75 µm) mesh (total mesh surface area 2.7 cm^2). Ag/AgCl (3 M KCl) was used as reference electrode (placed near to the surface of the hydrogel electrode) and carbon rod was used as counter electrode. All potentials were measured *vs*. Ag/AgCl). The electrolyte was continuously bubbled with Ar during electrochemical experiments for de-aeration.

Cyclic voltammetry (CV) experiments were carried out in potential range E = 0.4 to -0.85 V (except for redoping performed in 1 M H_2SO_4 solution, where E = 0.4 to -0.3 V) at scan rates 0.1–0.45 mV s^{-1} (fractal dimension) and 0.25 mV s^{-1} (redoping and specific capacitance measurements). Low scan rates were intentionally chosen to limit the redox current due to relatively smaller counter electrode surface area. Charge storage capacity was measured using linear sweep voltammetry experiments at a scan rate of 0.1 mV s^{-1} in aforementioned potential range, followed by long term (until redox current decay) chronoamperometry at final potential from total reduction charge and electrode dry mass. Specific capacitance was calculated as:[2] $C_s = (Q_a + Q_c) / (2\, m\, \Delta V)$, where Q_a and Q_c are oxidation and reduction charges, respectively; m the dry mass of hydrogel electrode and ΔV the potential window. Differential specific capacitance was also estimated from $C_m = I_{peak}\, \nu^{-1}\, m^{-1}$, where I_{peak} is peak redox current, ν is scan rate and m is dry mass of the hydrogel electrode. Both methods gave similar results, 159.1 and 154.8 F g^{-1}, respectively. Electrochemical impedance spectroscopy (EIS) experiments were conducted in AC frequency range from 1×10^{-4} Hz to 25 kHz at a constant potential of E = 0.4 V.

The type of mobile ion was determined from ECMD strain measurements. Displacement for calculating strain (relative change in thickness of gel electrode: $\varepsilon = \Delta L / L$, where ε is the strain, L is the initial thickness and ΔL the change in thickness) was measured using laser displacement meter LK-G82/LK-G3001P (Keyence). For displacement measurements, a piece of gold foil was placed on top of the hydrogel. The measured distance (change) was recalculated taking into account the refractive index of electrolyte. The hydrogel was electrochemically cycled in the target electrolyte for 96 h before performing the displacement measurements.

Density measurements

Due to the negligible shrinkage of aerogel extracted from Ac, the density was estimated based on volume of the extraction mould and weight of the aerogel. Semi-theoretical densities of the aerogels were calculated based on the measured doping levels (by EDX) under assumption that the reaction yield is limited only by the available oxidant. Then:

$$\rho = C_{Py} \times \left[1 - \frac{d_{DBS^-} + d_{SO_4^{2-}}}{2}\right] \times \left(W_{Py} - 2\times W_H + W_{DBS^-} \times d_{DBS^-} + W_{SO_4^{2-}} \times d_{SO_4^{2-}}\right), \qquad \text{(S1)}$$

where ρ is aerogels density, C_{Py} is Py concentration, d_{DBS} and d_{SO4} are DBS^- and SO_4^{2-} doping levels and W_{Py}, W_H, W_{DBS}, W_{SO4} are molar masses of Py, hydrogen, DBS^- and SO_4^{2-}, respectively.

Conductivity measurements. The electrical conductivity of the hydrogels and aerogels was measured with an in-house 4-point probe, according to Smits equation:[3] $\sigma = I \times (C'(a,d,s) \times F(w,s) \times w \times V)^{-1}$, where σ is the electrical conductivity, C' and F are correction factors depending on a (sample length), d (sample width), s (probe contact spacing) and w (sample thickness). I is the constant current applied between outer contacts of the probe, and V is the measured voltage on inner-contacts.

Low-temperature N_2 sorption measurements. The N_2 sorption experiments were performed at the boiling temperature of liquid nitrogen (-195.8 °C) using the ASAP 2020 system (Micromeritics). The specific surface area was calculated according to Brunauer-Emmett-Teller (BET).[4] Pore size distributions were obtained using non-local DFT using the slit-shaped pore model.[5]

Results

Monitoring polymerization using pH measurements. For 0.1 M Py-APS hydrogel, pH was measured during gelation (Figure S1c). It can be seen that at concentration 0.1 M Py-APS polymerization is almost complete after 1 h (no further significant evolution of H^+ ions from α-positions of the polymerizing Py units).

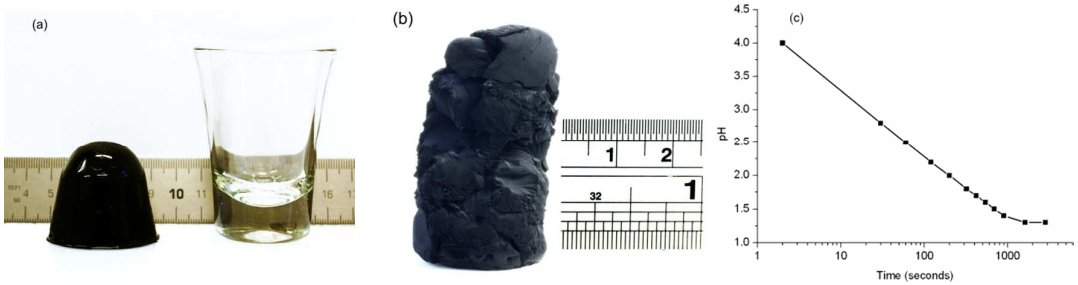
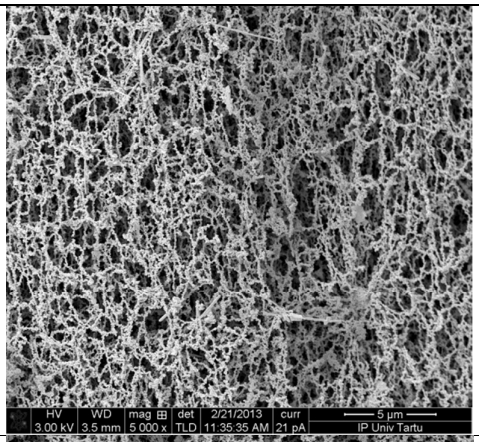
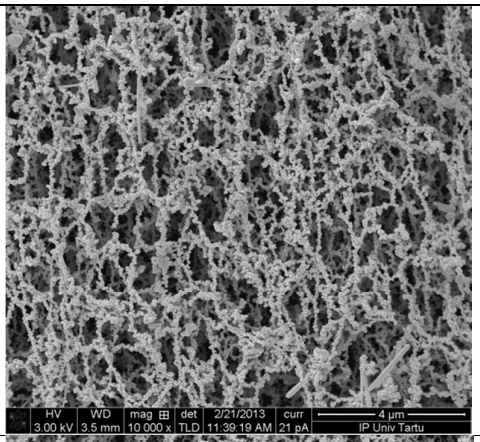
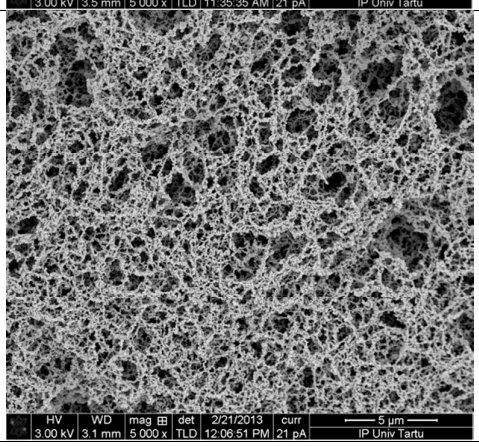
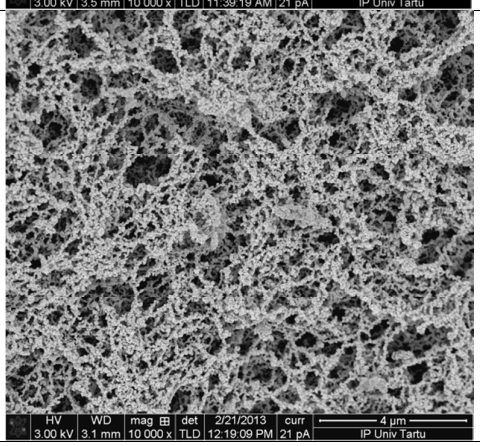
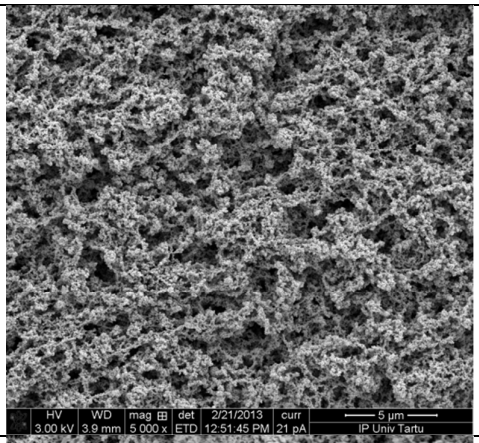
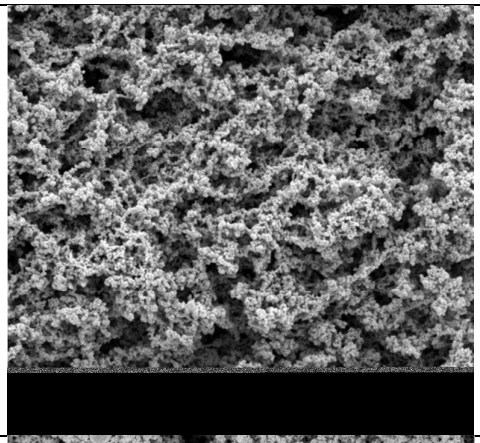
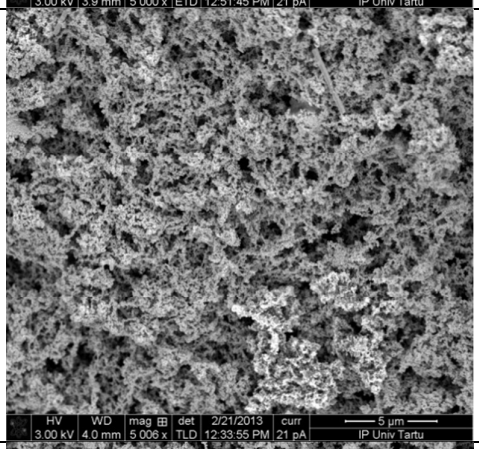
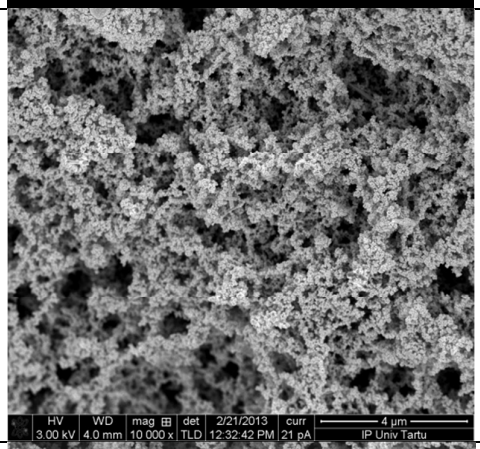
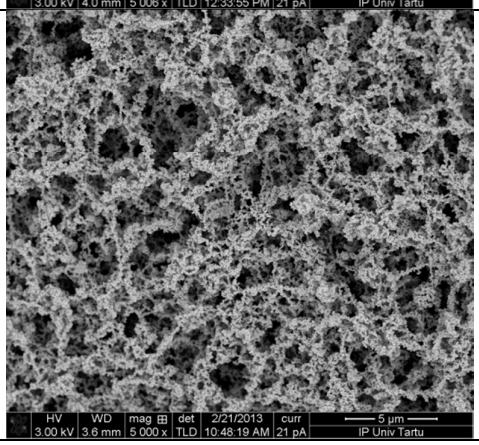
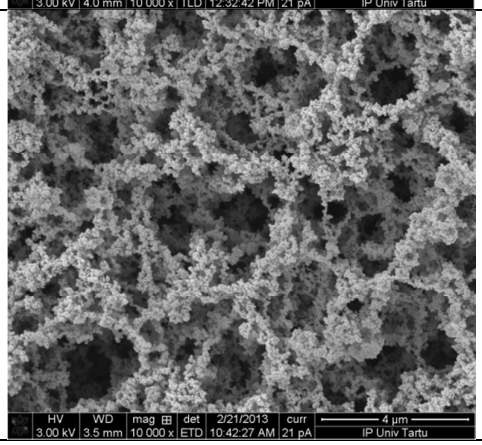


Fig. S1 PPy hydrogel and aerogels. (a) As prepared hydrogel (0.3 M Py-APS). (b) As-prepared PPy aerogel (0.2 M Py-APS). (c) Change in pH during polymerization of 0.1 M Py-APS hydrogel.

SEM micrographs

Py-oxidant concentration (M), oxidant	Magnification 5000×	Magnification 10,000×
0.1, APS		
0.2, APS		

0.3, APS		
0.3, SPS		
0.4, APS		

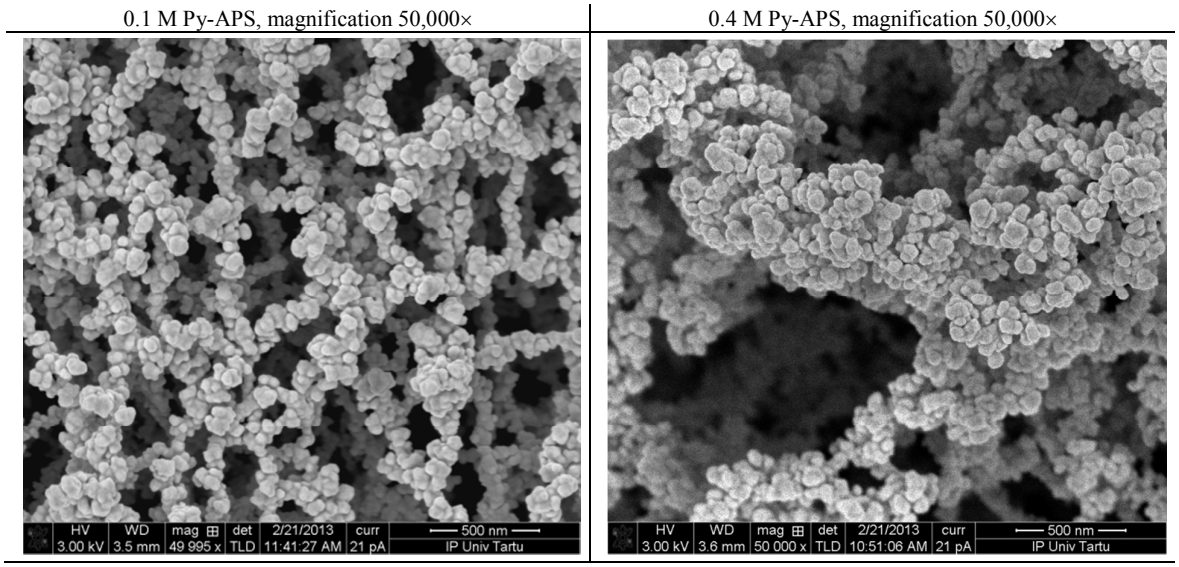


Fig. S2 SEM micrographs of PPy aerogels.

Ion mobility and fractal dimension

The mobility of various ionic species as a function of potential was ascertained using electro-chemo-mechanical deformation (ECMD) during cyclic voltammetry (CV) experiments. At the start of reduction cycle, the BF_4^- ions were found to diffuse out of the hydrogel leading to shrinkage of the hydrogel. Whereas at lower potentials, the Na^+ ions were found to diffuse into the hydrogel thereby compensating for the excess negative charge due to the less mobile DBS^- and SO_4^{2-} anions, hence leading to expansion of the gel.

Fractal dimension (d_f, Table S1) was calculated from CV experiments as $d_f = 2 \times \alpha + 1$, where α (faradic charge transfer coefficient) is the slope of the least-square fit of data points on the $\log(j_p)$ *vs.* $\log(\nu)$ graph (Fig. S3), j_p is the redox current density peak (mA cm^{-2}) and ν is the scan rate (mV s^{-1}).

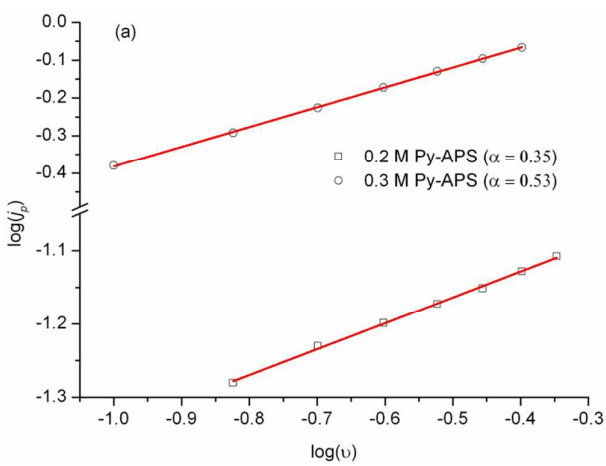


Fig. S3 Reduction peak current density $\log(j_p)$ *vs.* scan rate (ν) of 0.2 M Py-APS and 0.3 M Py-APS hydrogels and the corresponding least square fits.

Table S2 Charge transfer coefficients and calculated fractal dimensions.

Py-APS concentration (M)	α	Standard Error	R^2	d_f
0.2	0.35286	0.0064	0.99804	1.7
0.3	0.52569	0.0039	0.99967	2.1

EIS measurements

The results of the EIS (Fig. S4) showed that in the high frequency region of 20 kHz to 1 kHz, the impedance only slightly depends on the frequency indicating a pronounced ohmic behaviour, the series resistance (R_E) value of electrolyte and electrode was found to be 5.4 Ω (Fig. S4a, $f \approx 25$ kHz).

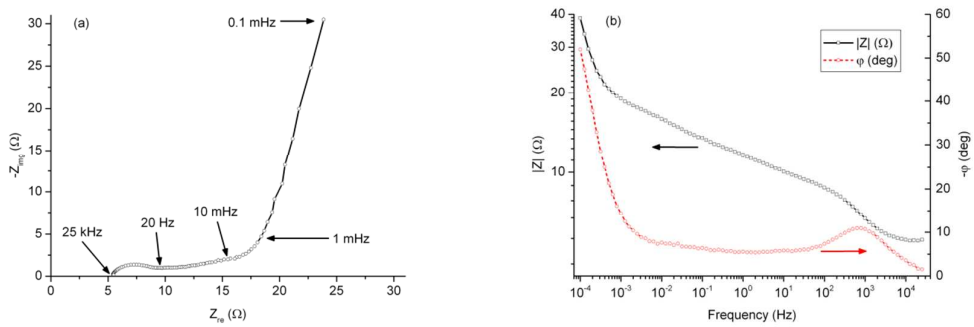


Fig. S4 EIS measurements of the 0.3 M Py-APS hydrogel in 0.2 M NaBF4 electrolyte. (a) Nyquist plot. (b) Bode |*Z*| and phase plot.

At frequencies from 10 to 0.01 Hz the Bode phase plot has broad minima denoting transition from charge transfer dominated process to the semi-infinite cylindrical diffusion at the interface of the electrolyte and polymer.[6] At low AC frequencies ($f < 1$ mHz), the linear, almost vertical Nyquist plot indicates nearly ideal capacitive behaviour. The value of phase angle below -21° (Figure S4b, Bode phase plot) and the sharp increase of |*Z*| (Fig. S4b, Bode |*Z*| plot) indicate mixed kinetics behaviour in accordance with the finite diffusion model (Ho *et al.*[7]) with finite reflective boundaries, that is characteristic of thin films.[8]

Aerogel's density and conductivity data and calculations

Table S3 Measured and calculated (eqn (S1)) density and conductivity of PPy aerogel as a function of Py and APS concentration.

Py-APS concentration (M)	Density (measured) (mg cm^{-3})	Density (calculated) (mg cm^{-3})	Conductivity (S cm^{-1})
0.1	12.8	13.5	2.4×10^{-5}
0.2	19.1	26.6	3.3×10^{-5}
0.3	24.7	37.9	1.6×10^{-2}
0.4	28.3	47.8	1.3×10^{-2}

Elemental analysis results and doping level calculations

Total doping level and different anion contributions were calculated from atomic ratios of N, S, O, B and Cl (nitrogen, sulphur, oxygen, boron and chlorine) from the elemental analysis.

Doping levels of aerogels

Table S4 Atomic ratios used for aerogel concentration-dependent doping level calculations.

Py-APS concentration (M)	Element (%)				Doping level		
	C	N	O	S	d_{DBS}	d_{SO4}	d_{sum}
0.1	79.89	8.76	8.58	2.77	0.285	0.031	0.316
0.2	78.77	8.77	9.48	2.98	0.278	0.062	0.340
0.3	78.16	9.43	9.48	2.93	0.238	0.073	0.311
0.4	77.19	10.07	9.79	2.96	0.204	0.090	0.294
0.3*	81.00	8.61	7.79	2.60	0.303	0	0.303

* Soluble PPy dried from Ac washing liquid of the hydrogel

Doping level calculations are based on the reasonable assumption (supported by the absence of Na in elemental analysis results) that after polymerization and washing the material contains only PPy - $(C_4H_3N)_n$, doped with DBS^- ($C_{18}H_{29}SO_3^-$ from NaDBS) and SO_4^{2-} anions (from APS) . As both anions contain one S atom, then the total doping level $d=d_{DBS}+d_{SO4}=(S_{DBS}+S_{SO4})/N$. S_{DBS} and S_{SO4} are derived from equations $O=3S_{DBS}+4S_{SO4}$ and $S=S_{DBS}+S_{SO4}$ (total number of oxygen atoms is sum of oxygen atoms from both anions and total number of sulphur is sum of sulphur from both anions). After solving both equations for S_{SO4} and equalizing both: $S–S_{DBS}=(O-3S_{DBS})/4$. Solving this equation for S_{DBS} gives $S_{DBS}=4S-O$. Replacing S_{DBS} to equation $S=S_{DBS}+S_{SO4}$ gives $S_{SO4}=O-3S$.

Doping levels of DBS^- and SO_4^{2-} and total doping level were calculated as:

$$d_{DBS^-}=\frac{4\times S-O}{N},\ d_{SO_4^{2-}}=\frac{O-3\times S}{N}\ \text{and}\ d_{sum}=d_{DBS^-}+d_{SO_4^{2-}}. \quad \text{(S2)}$$

Doping levels of hydrogels

1) 0.3 M Py-APS hydrogel redoped with BF_4^- by electrochemical cycling in 0.2 M $NaBF_4$ electrolyte.

Table S5 Atomic ratios used for doping level calculations of 0.3 M Py-APS hydrogel redoped with BF_4^-.

Element (%)					Doping level			
C	N	O	S	B	d_{DBS}	d_{SO4}	d_{BF4}	d_{sum}
77.12	10.16	9.34	2.84	0.54	0.199	0.081	0.053	0.333

Doping levels of DBS^-, SO_4^{2-}, BF_4^-, and total doping level were calculated as:

$$d_{DBS^-}=\frac{4\times S-O}{N},\ d_{SO_4^{2-}}=\frac{O-3\times S}{N},\ d_{BF_4^-}=\frac{B}{N}\ \text{and}\ d_{sum}=d_{DBS^-}+d_{SO_4^{2-}}+d_{BF_4^-}. \quad \text{(S3)}$$

2) 0.3 M Py-APS hydrogel redoped with ClO_4^- by electrochemical cycling in 0.2 M $LiClO_4$ electrolyte.

Table S6 Atomic ratios used for doping level calculations of 0.3 M Py-APS hydrogel redoped with ClO_4^-.

Element (%)					Doping level			
C	N	O	S	Cl	d_{DBS}	d_{SO4}	d_{ClO4}	d_{sum}
65.56	12.92	17.06	1.76	2.69	0.057	0.079	0.208	0.344

Doping levels of DBS^-, SO_4^{2-}, ClO_4^- and total doping level were calculated as (similar to eqn (S2), only O is replaced by (O-4Cl)):

$$d_{DBS^-}=\frac{4\times(S+Cl)-O}{N},\ d_{SO_4^{2-}}=\frac{O-4\times Cl-3\times S}{N},\ d_{ClO_4^-}=\frac{Cl}{N}\ \text{and}\ d_{sum}=d_{DBS^-}+d_{SO_4^{2-}}+d_{ClO_4^-}. \quad \text{(S4)}$$

3) 0.2 M Py-APS hydrogel redoped with SO_4^{2-} by electrochemical cycling in 1 M H_2SO_4 electrolyte. Doping levels are calculated according to eqn (S2).

Table S7 Atomic ratios used for doping level calculations of 0.2 M Py-APS hydrogel redoped with SO_4^{2-}.

Element (%)				Doping level		
C	N	O	S	d_{DBS}	d_{SO4}	d_{sum}
72.19	10.95	13.17	3.69	0.145	0.192	0.337

4) 0.3 M Py-APS hydrogel synthesized in 1 M HCl solution. Doping levels are calculated analogously to eqn (S2) (using Cl instead of B).

Table S8 Atomic ratios used for doping level calculations of 0.3 M Py-APS hydrogel synthesized in 1 M HCl solution.

Element (%)					Doping level			
C	N	O	S	Cl	d_{DBS}	d_{SO4}	d_{Cl}	d_{sum}
79.73	9.88	7.51	2.43	0.45	0.224	0.022	0.046	0.292

Low-temperature N_2 sorption measurements

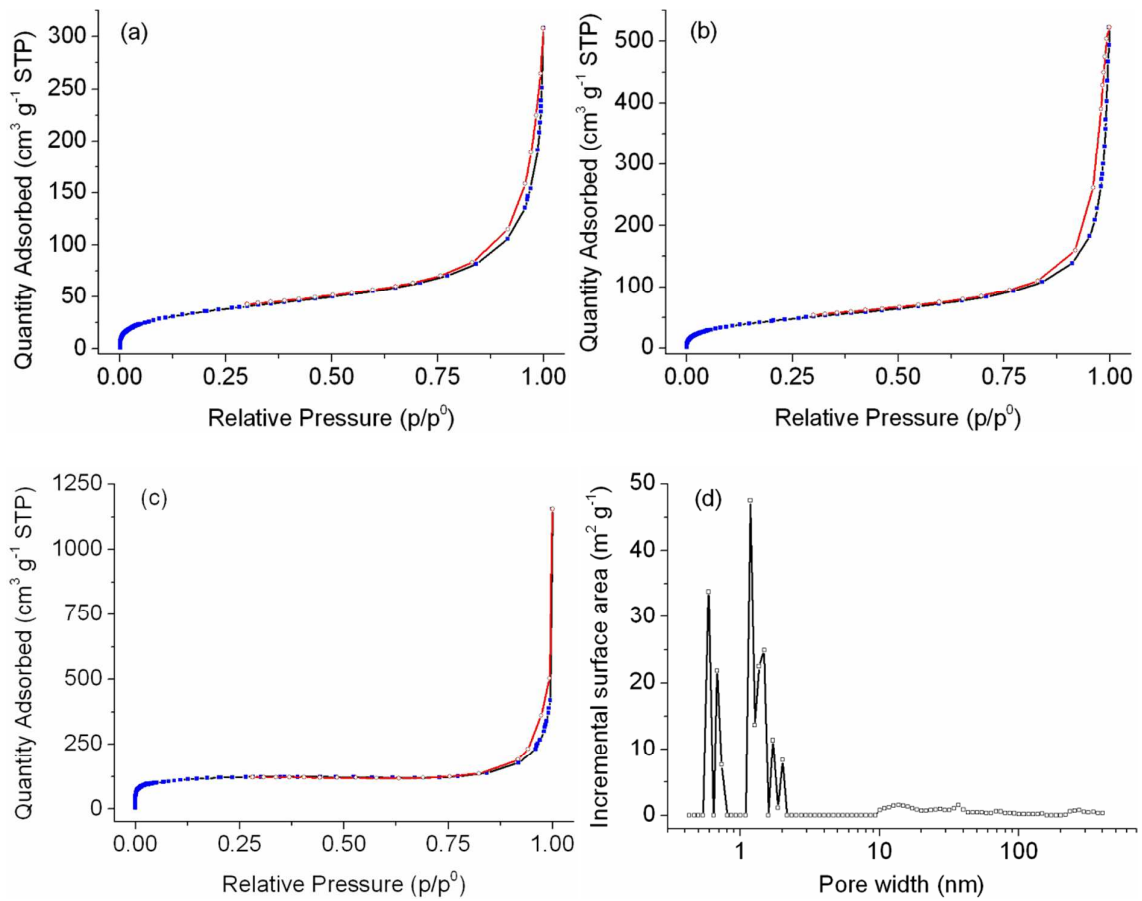


Fig. S5 Aerogel N_2 sorption isotherms (blue: adsorption, red: desorption): (a) 0.1 M Py-APS. (b) 0.3 M Py-APS. (c) Carbonized aerogel. (d) Incremental surface area (carbonized aerogel).

References

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3 F. M. Smits, *The Bell Syst. Tech. J.*, 1958, **May**, 711.
4 (a) S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **6**, 309; (b) F. Rouquerol, J. Rouquerol and K. Sing, *Adsorption by powders and porous solids: Principles, methodology and applications*, Academic Press, London 1999.
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8 R. Du and X. Zhang, *Acta Phys. Chim. Sin.*, 2012, **28**, 2305.

Reviewer(s)' Comments to Author:
Referee: 1
Comments to the Author
Dear Editor (and Authors),
I liked the content of this manuscript. The experiments were well planned. However...

The authors claim producing pristine sample as a result of their simple synthesis protocol without any supporting evidence of phase purity.

Indeed, the word “pristine” may carry several meanings depending on the subject. In the present case, „pristine“ is used in context of chemical composition, meaning that the structure of pyrrole units has not been unmodified and no additional linkers bind the chains together. This has been now clarified in the manuscript.
In the literature, the structure of PPy doped with any of the common anion species has been typically reported to be amorphous. There may exist supramolecular regularities in role of crystalline lattice, depending on Py/surfactant micelle size, which is controllable by monomer:surfactant molar ratio, temperature, chosen surfactant and monomer. Regularity may also appear on cluster size range. Further structural characterization is planned, but that would constitute incremental research which goes beyond the scope (and the short communication format) of the current manuscript.

Jyongsik Jang, Joon Hak Oh, *CHEM. COMMUN.* , 2002, 2200–2201
H. S. Nalwa, *Handbook of Organic Conductive Molecules and Polymers*, 1st edn., John Wiley & Sons, Chichester, England, 1997, vol. 3, p. 38.

Their experimental density does not match with their theoretical calculations, which they attribute to large solubility of the sample in acetone. It is hard to believe that this is purely a processing artifact.

We generally agree with the reviewer. Incomplete polymerization or polymerization to water-soluble non-contiguous oligomers can be another cause for the density difference and this cause is not enough emphasized in main text (reference to water-soluble unreacted Py, detached Py oligomers and remains of SDBS and oxidant is only in ESI). Increasing discrepancy with increasing concentration can be justified by hindered diffusion in denser hydrogels.

Calculated density is semi-theoretical due to the experimental doping levels used in the calculations and is based on the assumption that the polymerization yield depends on available oxidant only (due to oxidant deficiency condition). These limitations were expressed in the manuscript (supplementary material).

The reliability of the calculated doping levels was cross-checked based on S, C and N atomic ratios (calculations are in the answer to the next question) instead of S, O and N. The results were rather similar. Thus, we see three sources for discrepancy: lower than expected polymerization yield, partial solubility of low molecular weight components in water, and the solubility of higher molecular weight DBS^- doped fragments in acetone. We see the discrepancy and its dependence on concentration not as a calculation or measurement error, but rather as a measure of the overall gelation efficiency. Wording has been improved to express this point more clearly.

It is not clear to me how they arrived at the equations for calculating the doping levels. The equations containing multiplication and subtraction symbols without any brackets was confusing. Moreover, there were simple mathematical errors in all their tables- S3 through S7.

Calculations are based on a reasonable assumption (supported by absence of Na in elemental analysis results and coherence of the following results) that after polymerization and washing the material contains only PPy - $(C_4H_3N)_n$, doped with DBS^- ($C_{18}H_{29}SO_3^-$ from NaDBS) and SO_4^{2-} anions (from APS). Doping levels can then be calculated from atomic ratios of all combinations of 3 elements (S:O:N, S:C:N, C:N:O, O:S:C), leaving out the 4th measured atomic ratio. Only calculations based on the S:O:N combination are presented, but the remaining 3 were used for cross-checking (S:C:N in particular) and reliability confirmation. As both anions contain one S atom, the total doping level is $d=d_{DBS}+d_{SO4}=(S_{DBS}+S_{SO4})/N$.

A short explanation:
1) S:O:N (leaving out C): S, O and N are measured, S_{DBS} and S_{SO4} are derived from equations $O=3S_{DBS}+4S_{SO4}$ and $S=S_{DBS}+S_{SO4}$ (total number of oxygen atoms is sum of oxygen atoms from both anions and total number of sulphur is sum of sulphur from both anions). After solving both equations for S_{SO4} and equalizing both: $S-S_{DBS}=(O-3S_{DBS})/4$. Solving this equation for S_{DBS} gives $S_{DBS}=4S-O$. Replacing S_{DBS} to equation $S=S_{DBS}+S_{SO4}$ gives $S_{SO4}=O-3S$.

2) S:C:N (leaving out O): PPy has C_4 and N, DBS^- has C_{18}. Then $S_{DBS}=(C-4N)/18$ (for DBS^- ions remains C-4N carbon atoms and $S_{DBS}=C_{DBS}/18$) and $S=S_{DBS}+S_{SO4}$.

Similar approach was used for the C:N:O and O:S:C combinations.

If PPy is additionally doped with ClO_4^- anions then less oxygen is available for DBS^- and SO_4^{2-} and in (1) “O-4Cl” instead of O is used.

Usage of brackets and arrangement in formulas has been changed to improve readability, but it seems the use of brackets is not justified where the order of operations is clearly determined without them.

The presented doping levels are indeed different from those calculated from atomic ratios in same table. The reason is that we followed too strictly the journal’s policy (http://www.rsc.org/images/Author_guidelines_tcm18-186308.pdf p 4.3.5) that presented atomic ratios must be rounded to 0.1% precision. Doping levels were calculated from full-precision values. In order to adjust this controversy, an additional significant digit has been presented for the tabulated atomic ratios, the doping levels have been presented with lowered precision as calculated from the tabulated atomic ratios.

The authors kept changing from present tense to past tense, some times even in the same paragraph. Ok, English not being their first language, but the language in its current form is unacceptable for this journal.

We thank reviewer for the enormous work done with the manuscript. We regret the quality of our English and hope that the quality of the content somewhat balances the deficiencies in the English language.

My additional comments/corrections are marked in the attached pdf document. I have I am happy to accept this manuscript for publication if the authors

address my questions/queries and fix the manuscript accordingly, including language.

The vast majority of corrections have been introduced into the manuscript as proposed and gratefully acknowledged.

Comments:

“is it defects or agglomeration that led to larger voids -please see figure S2 for 0.4 APS at 10,000 X. Rewrite accordingly.” With “PPy chain defects and shorter conjugation” we considered polymerized and conjugated PPy chains itself, not chains aggregated from PPy particles. Wording has been improved.

“becoming more anion-exchanging” - Meaning of this sentence was that during the CV experiments anion mobility increased.

ESI: Added Table S1 and improved wording. We think that the misunderstanding was caused by the introduction of molar ratios, while we actually operated only with absolute concentrations.

ESI: “changed the colour of hydrogel from dark blue to pale” Not corrected in proposed form, as colour of the hydrogel did not change. It was the Ac used for washing that obtained blue colour, which become paler with every washing cycle. Elemental analysis (now Table 2 last row) showed that the blue colour originated from DBS-doped PPy fragments.

ESI: “Please confirm if it is V/s and not mV/s.” Fig S3 and the used scan rates were compliant (0.1-0.45 mV s^{-1}), but in the calculations we indeed found some inaccuracy. All the calculations have been re-checked, Fig. S3 and Table S1 (now Table S2) have been corrected and one of the fractal dimensions in the main text changed (from 2.2 to 2.1). The conclusions, however, remain the same.

Referee: 2
Comments to the Author
This manuscript reported a direct chemical method for preparing pristine polypyrrole (PPy) hydrogels and derived aerogels with high specific surface area. Moreover, their properties can be tuned by synthesis conditions and exchange of the dopant. The study is largely well carried out, and it is possibly suitable to be published in Journal of Materials Chemistry A. However, some critical problems should be addressed before this work can be accepted for publication.

(1) Page 2 lines 39-41, "The measured densities of the aerogels depending on reactant concentrations (12.8???28.3 mg cm-3) were somewhat lower than expected (13.5???47.8 mg cm-3)." The authors should give a reasonable explanation.

We understand the concern of the reviewer. In addition to the already described solubility in acetone, the incomplete polymerization or polymerization to water-soluble non-contiguous oligomers can be another cause for the density difference and this cause is not enough emphasized in main text (reference to water-soluble unreacted Py, detached Py oligomers and remains of SDBS and oxidant is only in ESI). Increasing discrepancy with increasing concentration can be justified by hindered diffusion in denser hydrogels.

Calculated density is semi-theoretical due to the experimental doping levels used in the calculations and is based on the assumption that the polymerization yield depends on available oxidant only (due to oxidant deficiency condition). These limitations were expressed in the manuscript (supplementary material).

The reliability of the calculated doping levels used in density calculations was cross-checked based on S, C and N atomic ratios instead of S, O and N. The results were rather similar.

The possible causes for lower measured density include the lower-than-expected polymerization yield, partial solubility of low molecular weight components in water, and the solubility of higher molecular weight DBS^- doped fragments in acetone. Increasing discrepancy with increasing concentration can be justified by hindered diffusion in denser hydrogels.

We see the discrepancy and its dependence on concentration not as a calculation or measurement error, but rather as a measure of the overall gelation efficiency. Wording has been improved to express this point more clearly.

(2) Page 2 line 73, "Specific surface area and pore size distribution of the aerogels (Fig. 3) were characterized by low-temperature N2 sorption method." The authors should provide their N2 sorption isotherms with pressure vs N2 uptake.

N_2 sorption isotherms have been added to ESI as Fig S5 (a-c).

(3) Page 3 lines 7-8, "The most significant difference is the peak (Fig. 3a,b) at pore width in range of 1???2 nm". In fact, there are a lot of differences in the pore size p < 300 nm.

Indeed, there are many quantitative differences, but in general the peaks follow the same pattern. From our point of view, the most significant qualitative change is peak shift between 1 and 2 nm. Wording has been improved.

(4) Page 3 lines 15-16, "the surface area increased from 134.4 to 425.8 m2 g-1 (see also Fig. 3d) ". Actually, it is difficult to see "the surface area increased from 134.4 to 425.8 m2 g-1" in Fig. 3d.

Two different methods were used for the N_2 sorption measurements. Total surface area was presented as BET area, porosity data was based on DFT. DFT-based cumulative area is somewhat misleading, but presented for the sake of better comparison with the literature (21), where both, differential and cumulative areas were presented. Wording has been improved to emphasize that the purpose of DFT was to describe the porosity distribution and allow comparison of different aerogels. Misleading reference to Fig. 3d has been removed.

(5) In addition, in Fig. 3c, it looks the surface area is up to 3000 m2 g-1 for the 0.1 M Py-APS derived carbon aerogel. The authors should explain it.

Differential surface area in Figure 3c was calculated as dS/dlog(D) and the value 3000 m^2 g^{-1} does not express the total surface area. **Differential** and cumulative surface areas were presented for better comparison with literature data (21). In the referenced paper, the differential area peak is higher than the total area as well. The reviewer probably was looking for **incremental** surface area. The incremental surface area graph has been inserted as ESI Fig S5d.

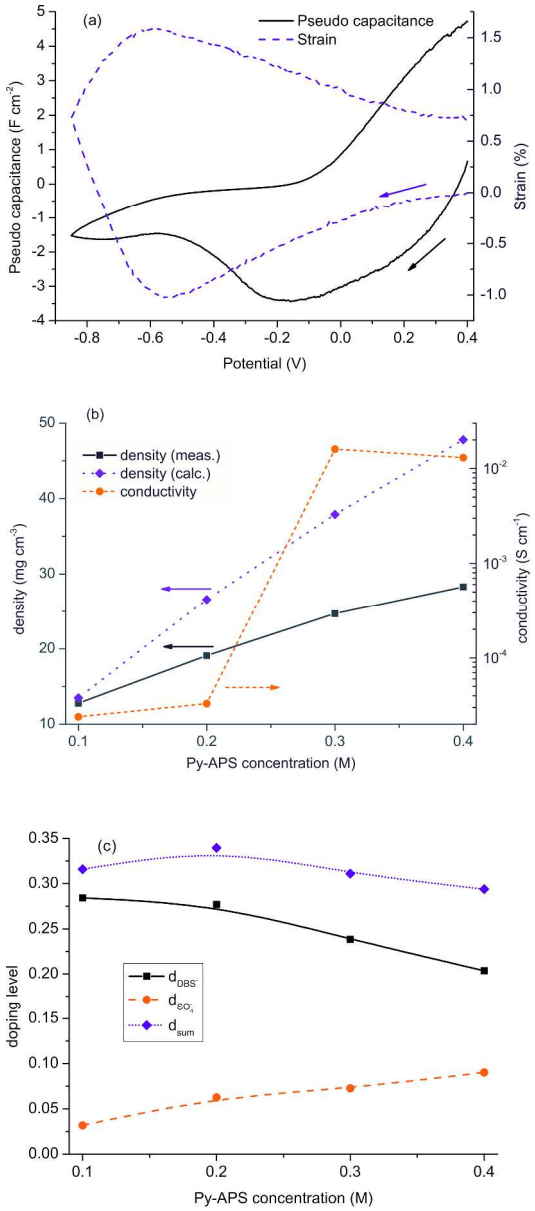

Fig. 2 (a) Electrochemical and ECMD measurements of the 0.3 M Py-APS hydrogel in 0.2 M NaBF4 electrolyte. Pseudocapacitance and strain (scan rate 0.25 mV s-1, surface area 18 cm2). (b) Measured density (squares), calculated density (diamonds) and conductivity (circles), also ESI Table S3–S4). (c) Contributions of DBS- (squares) and SO42- (circles) anions to total doping of aerogels.
186x424mm (600 x 600 DPI)