Electronic Supplementary Information

Experimental Section

All reagents used, including monomers were of analytical grade from Aldrich (Germany). Pyrrole monomer was purified before use by passing through Al_2O_3 microcolumn, 3,4-ethylenodioxythiophene was used as received.

In electropolymerization, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) experiments, a galvanostat-potentiostat CH-Instruments model 760A (Austin, TX) was used. Glassy carbon (GC) electrode (0.07 cm^2) as a working electrode, platinum sheet (area close to 0.5 cm^2) as the counter electrode and the double junction silver/silver chloride reference electrode with 1 M lithium acetate outer sleeve (Möller Glasbläserei, Zürich, Switzerland) were used.

Emulsions were prepared using homogenizer Hielscher, model UP 200S. To introduce monomers to microspheres ultrasonic washer Sonic 2 (Polisonic, Poland) was used. The obtained nanospheres were separated from the solutions using centrifuge MPW-251 Centrifuge (MPW Med. Instruments, Poland).

To obtain SEM images of prepared nanospheres Merlin instrument (Zeiss, Germany) was used. The chamber pressure was 1×10^{-5} Torr and the pictures were registered using 3 and 15 kV electron beam energies. To obtain TEM images of prepared nanospheres TEM Zeiss LIBRA 120 (HT =120 kV, LaB6 cathode) apparatus was used. Raman confocal microscope (Horiba–Jobin Yvon), equipped with an LPF Iridia edge filter, a 600 groove mm-1 holographic grating, and a 1024-256 pixel Peltier-cooled Synapse CCD detector was used. The microscope attachment was based on an Olympus BX41 system with an MPLN50x objective and a computer-controlled motorized x-y-z stage. The excitation source for the Raman measurements was a LION semiconductor laser (Sacher Lasertechnik) operating at 784.7 nm. Malvern Zetasizer Nano ZS (scattering angle 173 degrees) was used to evaluate zeta potential of nanospheres in DI water suspension (0.35 mg nanosphers /ml, pH close to 6.5).

Four point conductivity measurements were performed using a Jandel RM3 Microposition Probe (UK). Potentiometric experiments were performed using standard potentiometric setup and a multi-channel data acquisition setup and software (Lawson Labs, Inc., 3217 Phoenixville Pike, Malvern, PA, USA)[13].

Poly(n-butyl acrylate) microspheres were synthesized as described earlier[5b,13]. A mixture of n-butyl acrylate (480 µl), 1,6-hexanedioldiacrylate (220 µl) and 2,2-dimethoxy-2-phenylacetophenone (25 mg) was prepared and then it was dispersed in 5 ml of aqueous 1% (w/v) poly(vinyl alcohol) (PVA) solution with an aid of homogenizer (5 min, cycle 0.5, power 70 %). Polymerization step was conducted under argon atmosphere for 5 min using vigorous stirring of the emulsion (UV lamp of peak output 360 nm). Following polymerization, the spheres were separated using centrifugation at 5800 rpm for 15 min and were suspended in 5 ml portion of 1 % PVA.

Synthesis of nanospheres: 432 µl of pyrrole or 60 µl of 3,4-ethylenedioxythiophene (EDOT), was dissolved in 5 ml of deionised water using ultrasound bath (2 min, cycle 0.5, power 70 %). Then 1 ml of poly(n-butyl acrylate) spheres dispersion was added and the solution was transferred to ultrasonic bath for 20 minutes. Thus obtained suspension of monomer (pyrrole or EDOT) loaded microspheres was placed on a stirrer and 3 ml of oxidant solution (0.1 M for pyrrole or 1 M for EDOT oxidation sodium persulfate or 0.1 M iron (III) nitrate adjusted with HNO_3 to pH=1.27) was added, the mixture was left for 16 h, on the stirring plate. To highlight the benefits of this approach in the comparison synthesis 10^{-3} M sodium dodecylsulphate was present.

The resulting mixture was centrifuged (3500 rpm, 15 minutes) to separate bulky particles, the obtained supernatant was again centrifuged (18000 rpm, 30 minutes) to separate nanospheres from the polymerization mixture. The nanospheres obtained were dispersed in deionized water, again centrifuged and again dispersed in deionized water. The concentration of obtained nanospheres was 70 mg/ml.

Thus obtained nanospheres were placed on metal support for SEM analysis, on TEM grits, or deposited on GC electrode (10 µl of nanospheres suspension in water was used) and were left to dry in the room atmosphere.

Potentiostatic polymerization of pyrrole was performed at 0.9 V, from 0.5 M monomer and 0.1 M $Na_2S_2O_8$ or 0.1 M $Fe(NO_3)_3$, yielding elPPy-SO_4 or elPPyNO_3, respectively; polymerization charge was 5mC. Galvanostatic polymerization of EDOT was performed using anodic current $1.4.10^{-5}$ A, from 0.01 M monomer and 1 M $Na_2S_2O_8$, polymerization charge was 10 mC, yielding elPEDOT.

In Figure 1 and 2 currents for elPPySO_4 or elPPyNO_3 were recalculated to have the same oxidation charges for respective polypyrrole nanospheres. Cyclic voltammamogram was recorded in 0.1 M KNO_3, scan rate 50 mV/s. Impedance spectra were recorded at 0.5 V in 0.1 M KNO_3, amplitude 0.05 V.

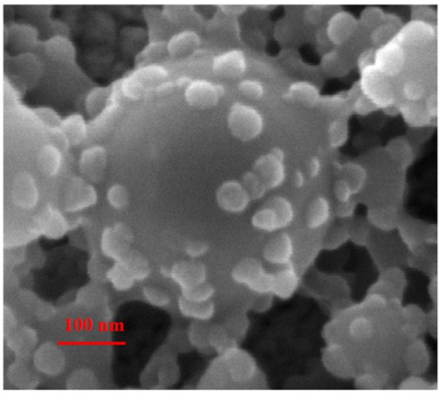
The layer of nanoPPyFe was obtained by drop casting 30 µl of nanospheres suspension containing 0.7 mg conducting polymer into the laser printed square 4mm × 23 mm on commercially available polyacetate foil intended for laser printers, as described previously[14a, b], Fig S3. After drying the layer was tested using four probe device or used further to prepare potentiometric sensor. To obtain potentiometric sensor a part of this shape was covered by drop casting 30 µl of potassium selective membrane cocktail containing (in wt.%) 1.1% of potassium tetrakis(4-chlorophenyl)borate, 2.8% valinomycin, 65.0% bis(2-ethylhexyl) sebacate and 31.1% poly(vinyl chloride); total 200 mg of membrane components were dissolved in 2ml of tetrahydrofuran. The rest of the nano-polypyrrole layer was isolated from the solution using PTFE adhesive tape. After conditioning for 24 h in 0.1 M KCl the potential dependence was recorded in KCl solutions.

Monomer pyrrole absorption experiments were performed for poly(n-butyl acrylate layers) prepared from mixture of n-butyl acrylate (480 µl), 1,6-hexanedioldiacrylate (220 µl) and 2,2-dimethoxy-2-phenylacetophenone (25 mg) by application of 20 µl of this mixture on the surface of commercial xerographic foil followed by 5 minutes photopolymerization, then the layer obtained was dipped in liquid pyrrole.

Fig. S1A (ESI†) is clearly showing different sizes of nanospheres

‘‘growing’’ directly on the surface of a microsphere. Since the monomer is available only at/close to the microsphere surface and the solution contains the oxidizing agent, further growth of the conducting polymer nanospheres in solution is not possible. It should be stressed that in the absence of microspheres, i.e. when the monomer is directly introduced to the solution, an amorphous polymer is formed, Fig. S1B in ESI.† In the following step the nanospheres can be separated from the polymerization mixture using centrifugation.

A.



B.

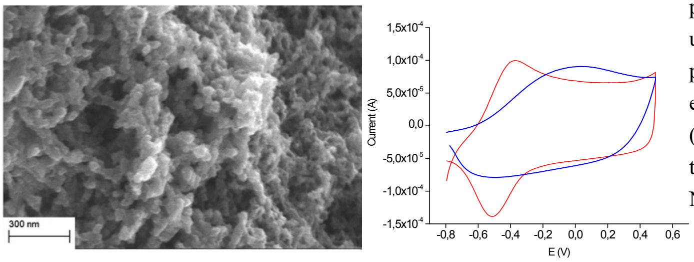


Fig S1

A. The SEM picture of polypyrrole nanospheres obtained by oxidation using $Fe(NO_3)_3$ showing gradual growth of nanospheres on the surface of microsphere.

B. The SEM picture of structure of polypyrrole obtained in course of polymerization performed in the absence of polyacrylic microspheres in the polymerization reaction, oxidation using $Fe(NO_3)_3$. The amorphous polymer was obtained, the structure is clearly and distinctly different from the polymer shown in Fig. 2. Cyclic voltammogram of (blue line) layer of amorphous polymer was compared to cyclic voltammogram (red line) of nanoPPy-Fe layer, as depicted in Fig. 2. The curve obtained for amorphous polymer shows wide and deformed peaks compared to polypyrrole nanoparticles. The current for amorphous polypyrrole was multiplied be a factor giving the same oxidation charge as for the nanoPPy-Fe. Oxidation charges are 1.4 and 19 mC for elPPy-NO_3 and chemically oxidized polymer (in the absence of polyacrylic microspheres), respectively.

Morphology of polymers obtained in the absence of microspheres and in the presence of microspheres used to deliver monomer to the polymerization solution are significantly different from results obtained for nanostructurized polypyrrole shown in Fig. 2.

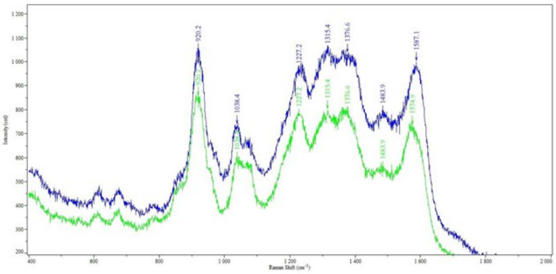


Fig 2S. The Raman spectra obtained for (blue line) nanoparticles nanoPPy-Fe and (green line) for electrochemically synthesized elPPy-NO_3.

As it can be seen form the Fig 2S. the same peaks/ peaks positions were observed both for polypyrrole in the form of nanospheres and for the electrochemically synthesized polypyrrole layer. Exactly the same position of obtained peaks is also a clear evidence of oxidized state of the polymer obtained in the form of nanoparticles.

A drop cast (from aqueous solution) dry layer of nanoPPy-Fe prepared on polyacetate foil was characterized with low resistivity, equal to 2 ohm sq^{-1}. Thus the nanoparticle suspension in water can be used for example, as a paint to obtain electrically conductive layers on other surfaces. The obtained low resistivity layers could be useful for e.g. sensor preparation purposes. The conductive layers obtained in this simple approach can be used as electrical leads and transducers to obtain disposable potentiometric sensors, using a similar approach to one reported by us earlier.[14] Thus the obtained potassium ion-selective electrodes, Fig. S3 (ESI†), after pre-treatment, were characterised with analytical parameters that compared well with classical arrangements (the slope was close to a Nernstian slope and it was equal to 54.5 mV dec, detection limit 10−5.7).

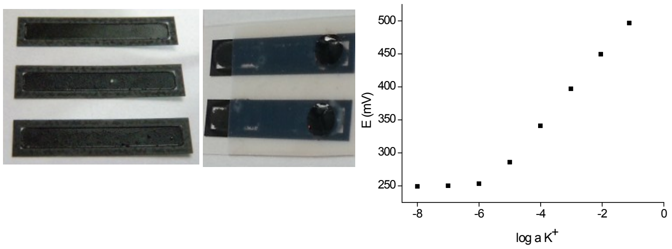


Fig S3. The picture of layer of nanospheres obtained on the polyacetate foil and the planar potentiometric sensor using nanoparticles (nanoPPy-Fe) as electrical lead and transducer (drop casted on polyacetate foil) and using potassium selective poly(vinyl chloride) membrane. The potentiometric responses – potential vs. log of activity of potassium ions in solution - of the fully equilibrated sensor are presented as well.

References

13 M. J. Ruedas-Rama and E. A. H. Hall, Analyst, 2006, **131**, 1282.
14 (a) A. Michalska and K. Maksymiuk, Anal. Chim. Acta, 2004, 523, 97;
(b) E. Jaworska, W. Lewandowski, J. Mieczkowski, K. Maksymiuk
and A. Michalska, Analyst, 2013, 138, 2363; (c) E. Jaworska,
M. Schmidt, G. Scarpa, K. Maksymiuk and A. Michalska, Analyst,
2014, 139, 6010.