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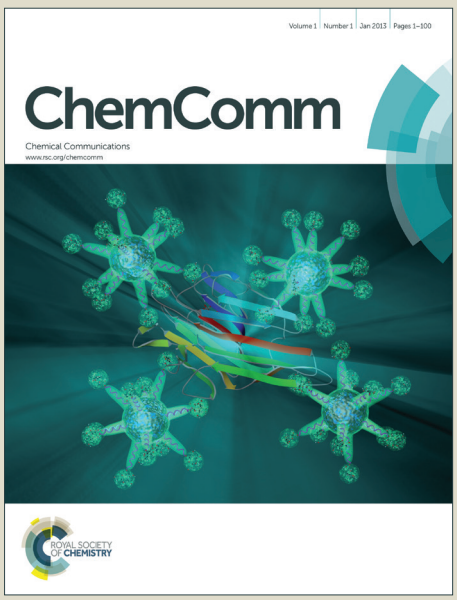

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Synthesis of conducting polymers nanospheres of high electrochemical activity

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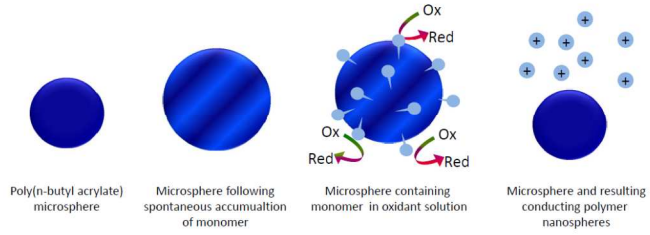
We propose a novel approach to obtain conducting polymers nanoparticles of high electrochemical activity and narrow size distribution. The method – templateless and seedless, uses polyacrylate microspheres to deliver monomer for polymerization reaction. Thus obtained nanostructures have active – unblocked – surface allowing fast charge/ion-exchange and form stable suspensions in water. Obtained nanostructures have potential to be applied in different fields ranging from conductive coatings and additives increasing electronic conductivity, to electrochemical sensors.

Conducting polymers are continuously drawing research attention, in recent years with a special emphasis on the nanoscale structures synthesis, properties and applications[1]. The proposed methods of conducting polymers (most often polypyrrole or polyaniline) nanoparticles synthesis include electrochemical or chemical oxidation of a monomer and often require application of templates (hard or soft) to confine the polymerization reaction in nanoscale[2]. The main disadvantage of this approach is necessity to release the obtained nanostructurized polymer from the template. To achieve this, after hard template synthesis (e.g. using track-etch polycarbonate or anodic aluminium oxide membranes) dissolution of the template under conditions that can adversely change properties of the nanostructures is required[3]. On the other hand, removal of soft templates which tend to permanently accumulate on the surface of nanostructures (e.g. surfactants or colloids) is often difficult, resulting ultimately in hindered or blocked ion-exchange and impaired electroactivity[4]. The presence of surfactants renders also electrochemical applications of conducting polymers[5a]. Other synthetic approaches, e.g. seeds or special precursors aided methods are often tailored and dedicated for particular polymers, moreover their use can also affect properties of resulting nanostructures in similar way[6]. Some conducting polymers can be formed also by an interfacial polymerization method performed in an immiscible organic/aqueous biphasic system, sometimes referred to as template-less synthesis[7]. This interfacial polymerization usually results in 1D nanostructures, regardless if they are polyaniline, poly(3,4-ethylenodioxythiophene) or polypyrrole[8,9]. Reports point out to fast redox switching of templateless synthesized nanomaterials (i.e. free from surfactants presence or necessity of template etching) and confirm that suspensions of such conducting polymers nanoparticles are stable in e.g. aqueous solutions[8,9]. Thus a synthesis method leading to 3D nanostructures of conducting polymers characterized with high electronic conductivity and unhindered ion-exchange is interesting for various applications, including electrochemical sensors[10]. In this work we present a novel simple method of templateless, seedless synthesis of con ducting polymer nanoparticles of high electrochemical activity and narrow size distribution, Scheme 1. It should be stressed that this method can be used to obtain nanospheres of different conducting polymers, using different oxidants. The obtained nanospheres can be easily separated from the reaction mixture in simple physical separation (centrifugation) step, without any special chemical treatment. The proposed approach does not require expensive reagents and is easily scalable, thus it can be interesting for different branches of modern science and technology.



Scheme 1. Schematic representation of proposed synthetic approach yielding highly electroactive conducting polymers nanospheres.

Herein proposed method can be foreseen as descendant of interfacial polymerization method and it benefits from ability of some polymers to spontaneously accommodate other liquids within their structure. The novelty lies in the idea to replace the water immiscible monomer solution by (polymeric) microspheres loaded with monomer/ solution interface. The idea of the proposed approach is schematically shown in Scheme 1. The polymeric microspheres, e.g.

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polyacrylate microspheres, can spontaneously accumulate other liquids on the expense of their swelling[11]. The experiments performed confirmed that poly(n-butyl acrylate) is especially good candidate for accumulation of monomers of conducting polymers being able to absorb about 250 % w/w of pyrrole with respect to its own mass within 10 minutes. Following accumulation, the monomer can be spontaneously and slowly released from the microsphere, through its pores. On the other hand charged oxidants e.g. Fe(III) cations or $S_2O_8^{2-}$ anions can hardly enter the ion-exchanger free polyacrylate microsphere. It was shown that even in the presence of ion-exchanger and selective receptor (ionophore) in the polyacrylate phase incorporation of charged ions into the sphere bulk is significantly hindered[5b,c] due to low ions mobility in the polymer. Thus the polymerization reaction occurs at the microsphere/ solution interface. The polyacrylate microspheres have negative zeta potential: for as prepared poly(n-butyl acrylate) microspheres obtained value was -11.7 mV. Absorption of monomer in the microsphere (in the amount as used for synthesis) leads to further decrease of zeta potential to -17.6 mV, with practically no change in the volume of microspheres dispersed in solution. When the microsphere containing monomer is transferred to a solution (e.g. containing oxidizing agent), the monomer is spontaneously released, due to simple partition equilibrium and its solubility in water. However, in the presence of excess of oxidizing agent in the solution, the monomer released is readily oxidized close/at the surface of the microsphere, positively charged oligomers are formed. Oligomers are expected to spontaneously adsorb on the surface of microspheres due to lipophilicity and electrostatic interactions. Indeed after 15 minutes of contact of microspheres with $Fe(NO_3)_3$ solution, when no nanospheres were formed yet as proven by SEM, the zeta potential of microspheres has increased significantly to be -4.3 mV. This significant change of zeta potential can be attributed to interaction of polyacrylate with oligomers of conducting polymer. It should be stressed that oxidation of oligomers occurs at lower potentials than oxidation of the monomer, assuring that under condition of monomer oxidation, they are positively charged. Taking into account availability of the monomer close to the microsphere surface and the presence of the oxidant, it can be expected that in time the amount of positive charge accumulated close to the microsphere surface will increase further due to elongation of conjugated backbone and progressing oxidation of released monomer. The latter process is rate limiting step taking into account excess of oxidant in the solution. Oligomers will spontaneously react to form less soluble in water structures and ultimately nanostructures. For $Fe(NO_3)_3$ used as oxidants some nanostructures were observed at SEM pictures taken after about 30 minutes – at that time the colour of synthesis mixture changed from light grey to black. With time the amount of structures observed on SEM image was increasing, however, the size of the nanospheres formed was similar. Ultimately the formed nanostructures of conducting polymer have high enough charge to overcome adsorption interactions due to electrical repulsion forces, between the microsphere with adsorbed oligomers and the nanostructure. The positively charged nanospheres will be "launched" into the solution. The positive charge carried by the oxidized polymer backbone assures stability of thus formed suspension. Indeed Fig S1A is clearly showing different size of nanospheres "growing" directly on the surface of a microsphere. Since the monomer is available only close to/ at the microsphere surface and the solution contains oxidizing agent, the further growth of 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, the amorphous polymer is formed, Fig. S1B in electronic supplementary information. In the following step the nanospheres can be separated from the polymerization mixture using centrifugation.

Clearly more detail studies related to mechanism of nanospheres formation are required, however, taking into account above proposed mechanism of the nanospheres formation, it can be expected that the key effect on the size of the formed nanostructures will be redox potential of the solution, charge of the oxidizing agent and ionic strength of the solution. The oxidation potential of the reagent used is setting the charge of the nanospheres being formed and thus controlling the "launch" charge. It can be expected that for the same microsphere polymer the lower oxidation potential, the bigger nanospheres are formed. Indeed for polypyrrole nanostructures synthesis change of the oxidant applied from $Fe(NO_3)_3$ to $K_3Fe(CN)_6$, for the same poly(n-butyl acrylate) microsphere and same amount of the monomer introduced to microspheres resulted in change of the nanospheres (predominant) diameter from about 30 nm to about 60 nm, respectively. On the other hand using as a starting material poly(vinyl chloride) commercial spheres (diameter close to 20 μm) and $Fe(NO_3)_3$ has resulted in nanoparticles of diameter close to 45 nm and using $K_3Fe(CN)_6$ as oxidant about 60 nm. It can be expected that due to the absence of traditional soft templates, the synthesis will result in nanoparticles benefiting from unhindered charge/ ion exchange and high electrochemical activity.

Figure 1A shows the SEM image of polypyrrole nanospheres obtained using sodium persulfate (nanoPPy-NaPS) as oxidizing agent. These nanospheres were separated from the polymerization mixture and polyacrylate microspheres in a simple centrifugation step. As it can be seen in Figure 1A the obtained nanospheres are characterized with regular spherical shape and relatively narrow size distribution – about 75 % of spheres have diameter close to 30 – 33 nm (50 % close to 30 nm and 25 % close to 33 nm). Figure 1B shows TEM image of obtained nanoPPy-NaPS. The histogram included confirms that majority of nanospheres has a diameter within the range from 30 to 36 nm (45 % - 33 nm). Nanostructures (without any additives) were forming a stable suspension in water. The zeta potential of suspension of nanoPPy-NaPS particles in deionized water was equal to 22 mV, confirming the oxidized state of polymer obtained. Figure 1C shows cyclic voltamogram (CV) of nanoPPy-NaPS layer (polymer doped by sulphate anions) obtained by simple drop casting of the nanomaterial dispersion on the glassy carbon (GC) electrode surface. It should be stressed that for potentials higher than -0.3 V the currents recorded were practically independent of the applied potential similarly as for electrochemically obtained layer tested in parallel. This constant current suggests capacitive behaviour of the obtained polymer, elPPy-SO_4, related to high ionic mobility and fast ion transfer at the polymer / solution interface. As a proof of concept confirming superior properties of spheres prepared using herein proposed approach (i.e. in the absence of surfactants) a curve recorded for a layer of nanospheres obtained using the same synthesis method, however in the presence of purposely added surfactant, is also shown in Figure 1C. Although, the amount of nanospheres forming the layer was comparable, the current recorded for the layer of nanospheres prepared in the presence of purposely added surfactant was significantly lower, suggesting impaired electrochemical activity. Figure 1D presents electrochemical impedance spectra (EIS) obtained for electrochemically synthesized polypyrrole film and a layer of nanoPPy-NaPS spheres obtained using herein proposed method, in the absence of surfactants. On these spectra small semicircles at high frequencies are visible, pointing to low resistance of the layers and high interfacial capacitance. For lower

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frequencies almost vertical lines were recorded, confirming bulk capacitive properties of both polymer layers.

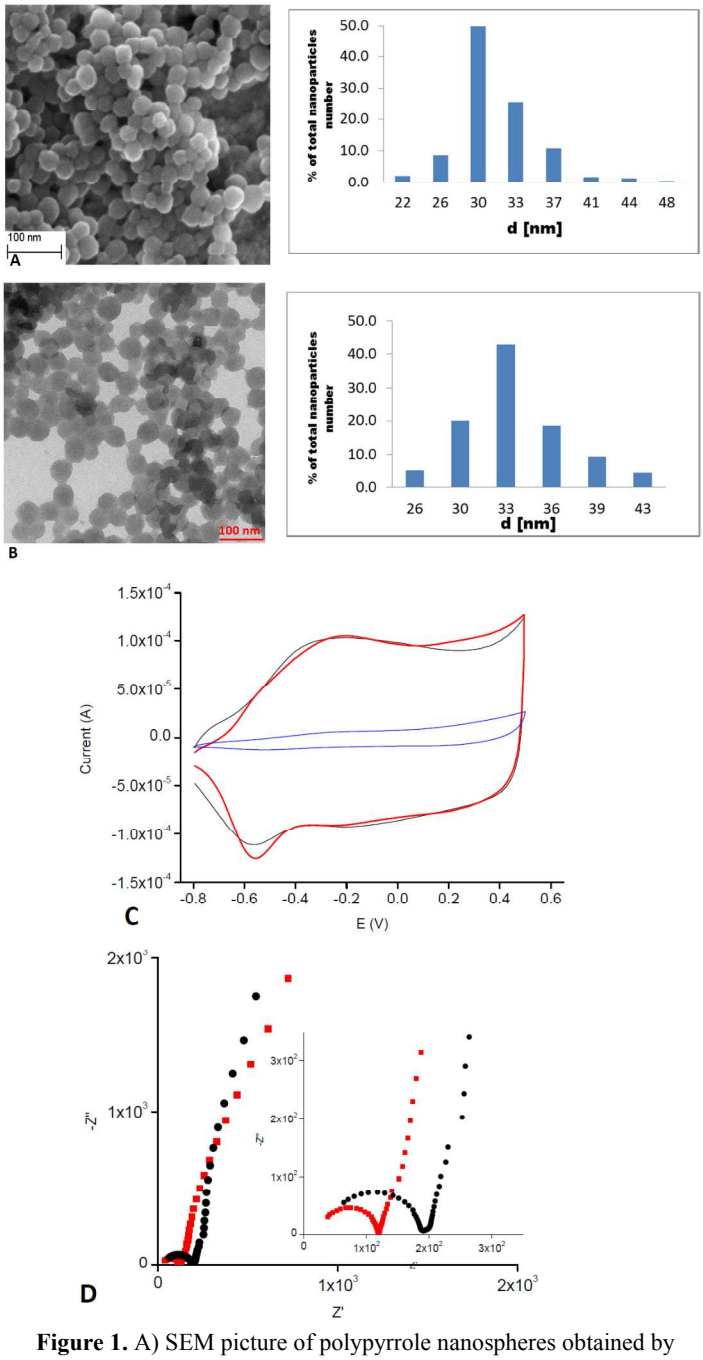

Figure 1. A) SEM picture of polypyrrole nanospheres obtained by oxidation using sodium persulphate and size distribution of obtained particles (ca 250 random nanospheres), B) TEM pictures of nanospheres and size distribution (ca 140 random nanospheres). C) Cyclic voltammograms of (red line) layer of nanoPPy-NaPS and (black line) layer of electropolymerizied polypyrrole, elPPy-SO_4. Oxidation charges are 2.1 and 1.1 mC for nanoPPy-NaPS and elPPy-SO_4, respectively. The current for elPPy-SO_4 was multiplied by a factor giving the same oxidation charge as for the nanoPPy-NaPS. Cyclic voltammogram of (blue line) layer of nanospheres obtained using microspheres aided monomer introduction to polymerization reaction, however, in the presence during synthesis of purposely added surfactant 10^{-3} M sodium dodecylsulphate. D) Impedance spectra of (red symbols) layer of nanoPPy-NaPS and (black symbols) elPPy-SO_4.

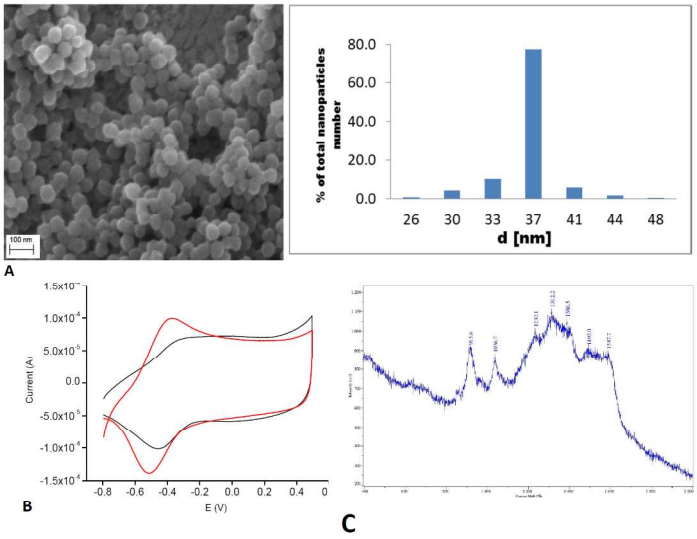

Figure 2. A) SEM picture of polypyrrole nanospheres obtained by oxidation using $Fe(NO_3)_3$ and size distribution of obtained particles (ca 320 random nanospheres). B) Cyclic voltammogram of (red line) layer of nanoPPy-Fe and (black line) layer of electropolymerized elPPy-NO_3. Oxidation charges are 1.4 and 0.40 mC for nanoPPy-Fe and elPPy-NO_3, respectively. The current for elPPy-NO_3 was multiplied be a factor giving the same oxidation charge as for the nanoPPy-Fe. C) Raman spectra recorded for a layer of nanoPPy-Fe.

Herein proposed method can be used to prepare nanostructures using also other oxidizing agents. Figure 2A presents SEM picture of polypyrrole nanospheres obtained by oxidation using $Fe(NO_3)_3$ (nanoPPy-Fe). As it can be seen in Figure 2A the obtained structures were slightly bigger compared to nanoPPy-NaPS. NanoPPy-Fe has regular spherical shape and narrow size distribution - about 80 % have similar diameter close to 37 nm. Following separation from synthesis mixture nanoPPy-Fe was forming stable suspension. The zeta potential of nanoPPy-Fe was equal to 32 mV, confirming highly oxidized character of formed nanostructures and their ability to form stable suspension. The voltammogram obtained for the layer of nanoPPy-Fe nanospheres shown in Figure 2B confirms high electroactivity with better shaped peaks at negative potential compared to the electrochemically obtained polymer doped with nitrate anions – narrower and higher peaks suggest higher uniformity of the material. The yield of polypyrrole nanoparticles synthesis was dependent on the oxidant used and for $Fe(NO_3)_3$ the total yield was 20 %, and for $Na_2S_2O_8$ total yield was close to 55 % Raman spectra recorded for nanoPPy-Fe show bands typical for polypyrrole[12]. The band at 1238 cm^{-1} can be assigned as the asymmetric in-plane C-H bending vibration. The bands at 1386 and 1588 cm^{-1} are associated with C-N and C=C stretching vibrations, respectively. Relatively small skeletal band is also seen at 1492 cm^{-1}. The bands in the range 900–1200 cm^{-1} are attributable to polarons and bipolarons.

To prove synthetic universality of herein proposed method nanospheres of poly(3,4-ethylenedioxythiophene) were also prepared using sodium persulfate as oxidant (nanoPEDOT-NaPS). Figure 3A presents TEM image of obtained nanoPEDOT-NaPS together with poly(n-butyl acrylate) microspheres used to deliver monomer to the oxidizing solution. Similarly as in the above described cases polymerization resulted in nanospheres of relatively small diameter, although slightly bigger compared to polypyrrole ones, the diameter

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of 65 % of nanospheres was close to 40 nm, Figure 3B. The cyclic voltammogram of the layer prepared from nanoPEDOT-NaPS is shown in Figure 3C. It shows almost rectangular shape indicating capacitive behavior of the layer, more exposed than for electrochemically obtained polymer doped with sulphate anions. This conclusion was supported by EIS results, where a vertical line at lower frequencies was recorded for nanoPEDOT-NaPS, confirming almost ideal capacitive properties of the nanostructurized polymer.

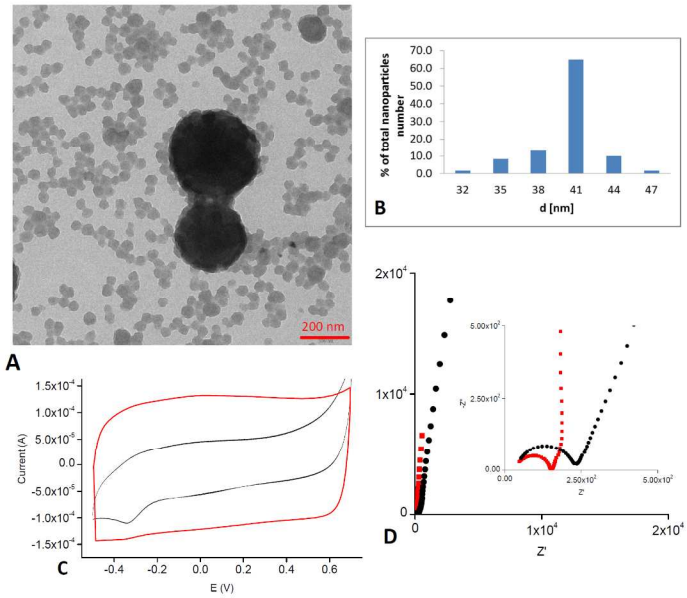

Figure 3. A) TEM picture of poly(3,4-ethylenedioxythiophene) nanospheres obtained by oxidation using sodium persulphate, B) size distribution of obtained particles (ca 60 random nanospheres). C) Cyclic voltammogram recorded in 0.1 M KNO_3, of (red line) layer of nanoPEDOT-NaPS and (black line) layer of elPEDOT. Oxidation charges are 2.9 and 0.2 mC for nanoPEDOT-NaPS and elPEDOT. C) Impedance spectra of (red symbols) layer of nanoPEDOT-NaPS and (black symbols) layer of elPEDOT.

The conducting polymer nanostructures obtained are potentially attractive for different applications, ranging from plastic (organic electronics), through catalysis to electrochemical sensors. 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. Thus the nanoparticles suspension in water can be used for example as paint to obtain electrically conductive layers on other surfaces. The obtained low resistivity layers can 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 similar approach to reported by us earlier[13]. Thus obtained potassium selective ion-selective electrodes, Fig S3, after pre-treatment, were characterised with analytical parameters well comparable with classical arrangements (slope close to Nernstian equal to 54.5 mV.dec, detection limit $10^{-5.7}$).

Conclusions

In summary, the synthesis of high electrochemical activity nanospheres of different conducting polymers was achieved by means of novel approach that utilizes polymeric microspheres to (spontaneously) release monomer to environment where it gets oxidized forming nanostructures. The synthesis conveniently is performed in water, it does not require expensive reagents and can be easily scaled up. The nanoparticles formed are obtained as stable suspension, they are characterized with a narrow size distribution and exhibit excellent electrochemical activity, due to absence of surfactants, colloids or seeding agents. The versatility of the proposed approach was confirmed by the application of different oxidizing agents and synthesis of polypyrrole and poly(3,4-ethylenedioxythiophere) nanoparticles.

Notes and references

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