CHEMISTRY OF MATERIALS

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Synthesis of Poly(3,4-ethylenedioxythiophene) Microspheres by Ultrasonic Spray Polymerization (USPo)

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Supporting Information

Poly(3,4-ethylenedioxythiophene), PEDOT, is a conjugated polymer that can be tailored to exhibit different electronic properties (i.e., insulating, semiconducting, metallic, semimetallic)[1,2] and has found a variety of applications including energy storage, photovoltaics, and LEDs.[3,4] The use of PEDOT as a supercapacitor material for energy storage originates in its ability to store charge both in the electrical double layer and throughout the body of the polymer by rapid faradaic charge transfer (pseudocapacitance). PEDOT is generally considered a superior supercapacitor within the field of conjugated polymers (e.g., vs polyaniline and polypyrrole) due to its chemical and thermal stability.[3]

Because the charging and discharging of PEDOT involves mass transport of counterions into and out of the polymer structure, slow ion diffusion is often the limiting factor in the efficiency of PEDOT-based supercapacitors (especially at high charge/discharge rates). One solution to this problem is to fabricate PEDOT electrodes with high surface areas via template-assisted approaches. Using templates such as surfactant micelles,[5−15] mesoporous silica,[16,17] silica microspheres,[18,19] or polystyrene,[20,21] a number of research groups have prepared PEDOT with nano/micrometer-sized structures. PEDOT nanotubes have also been prepared by sacrificial growth within anodized alumina pores and extensively investigated as supercapacitor materials;[22−24] the thinness of nanowires permits rapid ion diffusion, resulting in both high energy and power density. Sacrificial templates, however, are cumbersome and expensive. The ability to synthesize PEDOT micro/nanostructures in a template-free fashion could reduce synthetic steps and cost; so far, however, there are only a few reports on template-free morphologically control of PEDOT with only limited supercapacitive properties.[25−28]

Ultrasonic-spray-assisted materials synthesis is a one-step and continuous synthetic process. Ultrasonic nebulization produces micrometer-sized droplets that function as isolated microreactors.[29−32] To date, ultrasonic spray synthesis has been used to synthesize a diverse range of materials including metals,[33] ceramics,[34] metal oxides,[35] metal sulfides,[36] semiconductors,[37] and high-surface-area carbons[38,39] with control over various particle morphologies. Ultrasonic nebulization has had very limited use, however, for the synthesis of polymeric microspheres from monomers.[40]

In this paper, we report an ultrasonic spray polymerization (USPo) for PEDOT microspheres. These microspheres were formed by polymerization of nebulized microdroplets of solutions containing monomer 3,4-ethylenedioxythiophene (EDOT) and oxidant (Fe^{III} salts or sodium persulfate) that were then passed through a heated tube (150−170 °C, Figure 1). This process is free of template or added surfactant. Three types of PEDOT morphologies (porous, solid, and hollow) can be obtained by using different precursors and solvents. This ultrasonic spray polymerization of PEDOT is, to our knowledge, the first reported process that can continuously produce PEDOT microspheres with controlled morphologies. Because of the fact that the USPo process is facile, continuous, and single-step, this synthetic process is ultimately scalable for bulk synthesis and large rigs (2.5 m length, 150 kg/day) for ultrasonic spray pyrolysis have been constructed.[41] The synthesized microspheres are tested for their supercapacitance

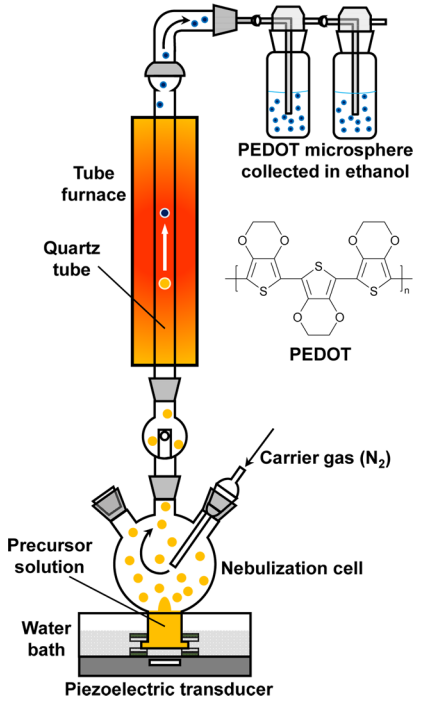

Figure 1. Ultrasonic spray polymerization (USPo) apparatus for the synthesis of PEDOT microspheres. The yellow precursor solution here illustrates a solution containing Fe^{3+} ions as oxidant with 3,4-ethylenedioxythiophene monomers.

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(160 F/g), which is among the highest reported for PEDOT-based materials.

The precursor solution containing EDOT and oxidant (e.g., 200 mM EDOT and 250 mM $FeCl_3$) was nebulized into micrometer-sized droplets and carried by nitrogen flow through the furnace tube that was preheated to the desired temperature (e.g., 150 °C). The monomer EDOT in each droplet polymerized upon heating. This radical cationic polymerization yields a conjugated backbone chain, polythiophene, with a dark-blue color.[3] The products are then collected in bubblers as a suspension in ethanol. The synthesized PEDOT microspheres have good dispersibility, with a zeta potential of +16 mV. No surfactant or template directing agent (which may affect PEDOT properties either by introducing impurities or damaging PEDOT structures) were used.

In general, there are only three morphologies possible for microspheres: solid, porous, and hollow. By controlling the choice of oxidants, we were able to produce examples of each of these morphologies. Oxidation of EDOT with iron(III) *p*-toluenesulfonate, $FeCl_3$, or sodium persulfate yielded solid, porous, and hollow microspheres, respectively (Figures 2, S1, and S6). During oxidation, EDOT forms linear polymers of PEDOT,[42] and polymerization induced by oxidation by Fe^{III} is much faster than by persulfate. Fe^{III} oxidants therefore form nanoparticles of PEDOT that aggregate, either nearly completely (which forms solid microspheres) or incompletely (which forms porous microspheres). In the presence of tosylate anions (which appears to act as a plasticizer), the nanoparticle aggregates of linear polymer intermingle during the USPo heating, resulting in relatively smooth, solid microspheres (Figures 2a,b and S6). When $FeCl_3$ is used, however, the blending of nanoparticles is incomplete and the resulting microspheres are porous aggregates of few nanometer-sized particles (Figures 2c,d and S6) with a BET surface area of 49 m^2/g, which is comparable to the surface area reported[15] of a nanoporous PEDOT film. In contrast to Fe^{III} oxidants, when sodium persulfate is used as an oxidant, the polymerization is slower and as the polymer is formed, it is excluded from the 50% ethanol/water core, forming an outer polymeric surface on the droplet (thus creating hollow microspheres, Figures 2e,f, and S6). By comparison, $FeCl_3$ oxidation in ethanol/water (vs ethanol only) still produces porous microspheres like those in Figure 2c,d. In all cases, the overall size of the microspheres is controlled by the precursor concentrations in the nebulized solution and the droplet size during nebulization (which is controlled by the ultrasonic frequency and the liquid surface tension[30,36−41])

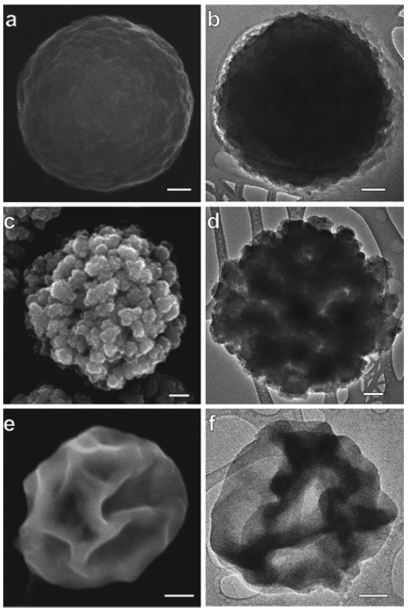

Figure 2. SEM (a, c, e) and TEM (b, d, f) of three different morphologies of PEDOT microspheres: (a, b) solid microspheres from $Fe(TsO)_3$ oxidation of 3,4-ethylenedioxythiophene in ethanol, (c, d) porous microspheres from $FeCl_3$ oxidation in ethanol, and (e, f) hollow microsphere from sodium persulfate oxidation in 50% ethanol/water. Scale bars represent 200 nm.

The chemical structure of the PEDOT microspheres was confirmed by FTIR (Figure S2), which is fully consistent with previously reported data.[43] Thermostability is confirmed with TGA analysis (Figure S3), showing that the major decomposition occurs around 300 °C.[3] In addition, these PEDOT microspheres are mostly amorphous polymeric material based on the absence of a characteristic peaks in powder XRD data (Figure S4).[44,45] Elemental analysis confirms the appropriate composition for PEDOT: C 50.5% (51.0 theor.), H 2.9% (2.9% theor.), and S 22.2% (22.8% theor.). Energy-dispersive X-ray spectroscopy (EDX) (Figure S7) also confirmed negligible presence of impurities (e.g., less than 0.5% Fe or Na).

Formation of PEDOT coatings has remained an interesting challenge.[46−49] The majority of existing approaches are electrochemical deposition or oxidative chemical deposition, which prove difficult to scale-up. We have found that one may readily convert the USPo process into a spray-coating technique simply by diverting the product gas flow to a direct exit through a nozzle (e.g., a pipette tip) onto a substrate of choice (e.g., silicon wafer, glass coated with FTO, or conductive fibrous carbon paper). For example, we used this spray-coating method to fabricate electrodes by spraying PEDOT microsphere onto fibrous carbon papers (Figure 3a). The coated substrates are followed by subsequent rinse and drying steps to remove residual impurities. Given the hydrophobicity of both PEDOT and carbon paper, the microspheres are well attached to the surface. One may also spray-coat flat surfaces in a controlled manner: Figure 3b is an enlarged image of spray coating of a flat surface (Si wafer), and Figure 3c shows a photo image of a masked spray pattern on colored glass.

The supercapacitor properties of PEDOT microspheres were evaluated by cyclic voltammetry (CV) and galvanostatic charge−discharge curves (with Ag/AgCl reference electrode and in 1 M $LiClO_4$ acetonitrile solution). The PEDOT microspheres exhibit CV scans with excellent supercapacitance even at very high sweep rates (Figures 4 and S5). The 10% decrease in the fill factor (from 50 to 1000 mV/s) is comparable to that observed with electrochemically deposited PEDOT films (Figure S8).[50] Symmetrical triangular shapes in galvanostatic curves (Figure S9a) are indicative of ideal capacitive behavior. The highest specific capacitance observed, 160 F/g, is obtained with PEDOT synthesized from $Fe(TsO)_3$ oxidation; this is comparable to prior supercapacitance measurements on PEDOT prepared using various templated methods.[51] Finally, a supercapacitor device was fabricated with symmetric PEDOT electrodes.[52] The specific capacitance of the observed with the symmetric PEDOT electrodes was half of the single electrode (measured by galvanostatic charge/discharge experiment, Figure S9b), as expected.

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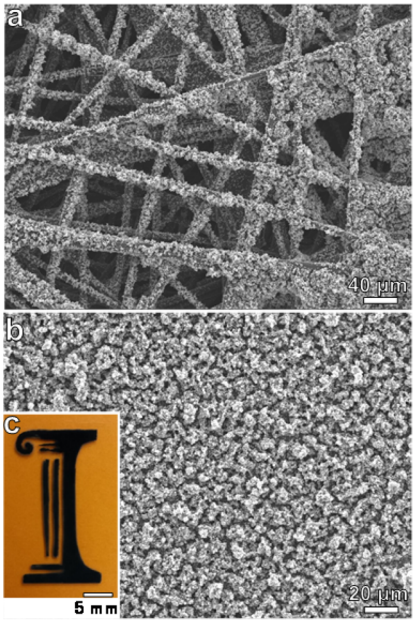

Figure 3. (a) SEM image of direct spray of PEDOT microspheres (from $FeCl_3$ oxidation) on carbon fiber paper, and (b) on silicon wafer. Both images are taken after the substrates are coated, washed, and dried under air. (c) Photo images of PEDOT patterning from masked spray coating.

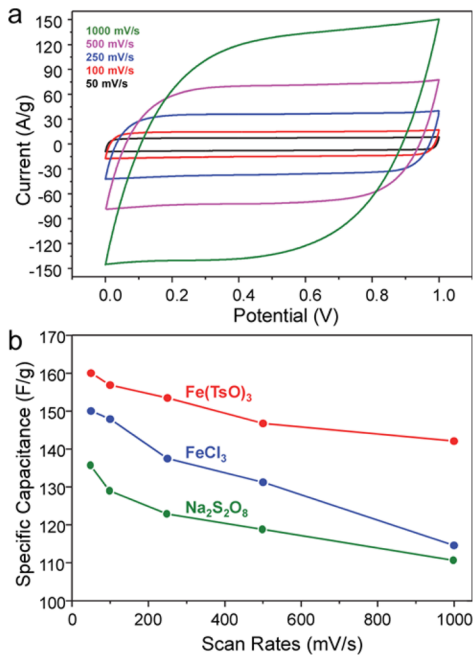

Figure 4. (a) Cyclic voltammagram of PEDOT microspheres synthesized from $Fe(TsO)_3$ oxidation. (b) Specific capacitance as a function of scan rate of PEDOT synthesized from $Fe(TsO)_3$, $FeCl_3$, and $Na_2S_2O_8$ oxidation, as labeled. The highest specific capacitance, 160 F/g, is observed with PEDOT synthesized from $Fe(TsO)_3$ oxidation.

The supercapacitor properties at high scan rates (>500 mV/s) of previously reported PEDOT microspheres generally suffer loss of ideality due to surfactant impurities or poorly conductive substrate coatings (such as SiO_2).[16] In comparison, PEDOT nanotubes have excellent supercapacitance even at high scan rates (e.g., 140 F/g with ideal charge/discharge behavior at 1000 mV/s), but are exceedingly difficult to prepare in quantity due to the prohibitive costs of the sacrificial alumina templates.[51] In our work here, USPo synthesized PEDOT possesses comparable specific capacitance (160 F/g) and good charge/discharge abilities and can be easily scaled up without templates or additional etching steps.

In summary, we have reported the synthesis of PEDOT microspheres by restricting the oxidative polymerization of EDOT in micrometer-sized droplets formed by ultrasonic nebulization. This method provides a facile, one-step, scalable process for bulk PEDOT synthesis.[41] We have successfully controlled microsphere morphologies (porous, solid, and hollow) by choice of oxidant and solvent in the precursor solutions. The microspheres were characterized with electron microscopies, FTIR, TGA, BET, and XRD. These PEDOT microspheres is potentially useful as supercapacitor materials by determining their specific capacitance of 160 F/g, which is among the highest yet reported. This synthetic method is amenable to facile spray-coating of conductive substrates (even textured substrates) and may potentially prove useful in the preparation of composite PEDOT microspheres, e.g., PEDOT-coated metal oxides, to increase the total specific capacitance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b03423.

Detailed description of the experimental procedure of using ultrasonic spray polymerization synthesis for PEDOT microspheres, materials characterization, instrumental information, electrochemical characterization, and other supporting data including low magnification SEM images, FTIR data, TGA data, powder-XRD data, cyclic voltammograms, galvanostatic test data (PDF).

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Notes

The authors declare no competing financial interest.

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