Green chemistry synthesis of nanostructured poly(2,5-dimethoxyaniline)

Sujit Jain,[a] Sumedh P. Surwade,[b] Srikanth Rao Agnihotra,[b] Vineet Dua,[b] Pamela A. Eliason,[c] Gregory J. Morose[c] and Sanjeev K. Manohar*[a]

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A compact, high surface area nanostructured poly(2,5-dimethoxyaniline) powder having high electrical conductivity ($\sigma \sim 10^{-1}$ S cm^{-1}) and high charge storage capacity (C_{sp} ~205 F/g) is synthesized in one step by chemical oxidative polymerization of 2,5-dimethoxyaniline using HCl/NaCl/H_2O_2 as a mild oxidizing system.

Introduction

The conventional chemical oxidative polymerization of aniline and its ring- and N-substituted derivatives yields a large family of polyanilines having interesting electrical, optical and electronic properties with significant technological potential.[1] Oxidants like $(NH_4)_2S_2O_8$, $FeCl_3$, KIO_3, $K_2Cr_2O_7$, *etc.*, are commonly used in the reaction consisting of aniline monomer dissolved in dilute aqueous acids (typically 1.0M HCl, pH~0).[2,3] There are several reports on greener, milder approaches, *e.g.*, by using H_2O_2 as the oxidant,[4-10] and by using polymeric dopants to keep the polymer chains doped at high pH.[11,12] The use of H_2O_2, however, frequently requires the use of a catalyst, *e.g.*, a H_2O_2/Fe^{2+} system was first used in 1910 to synthesize conducting parent polyaniline (emeraldine)[13] from aniline dimer and, more recently, to synthesize polyaniline nanofibers.[10] Enzymes like horseradish peroxidase (H_2O_2/HRP) were also used as mild catalysts in an effort to carry out the reaction at lower pH (pH 3-4 buffer).[6] We recently reported a high ionic strength system (HCl/NaCl/H_2O_2) that permits the use of H_2O_2 without any added catalysts to synthesize nanofibers of polyaniline and aniline oligomers in one step.[2] *We were surprised to find that broadening the use of this system to ring alkyl and alkoxy substituted derivatives was not straightforward*. In the case of 2-alkyl substituted anilines the reaction yielded low conducting granules (no nanofibers), and in the case of 2-alkoxy substituted anilines the reaction yielded brown insulating solids. We found that the optimum reaction conditions are different for different aniline derivatives when employing the HCl/NaCl/H_2O_2 system (henceforth termed "NaCl/H_2O_2") and in most instances no nanofibers are formed. We reasoned that unlike the head-tail coupling at the 4-position observed in unsubstituted aniline which takes place predominantly by an ionic mechanism, these electron donating 2-substituents activate the 3 and 5 positions as well. This could, in principle, favor a free-radical reaction pathway resulting in coupling at these positions in a head-head, or tail-tail fashion. In this study, we evaluated 2,5-dimethoxyaniline as a model system where the 5-position is blocked. Poly(2,5-dimethoxyaniline) is an important organic solvent soluble polyaniline derivative that has been synthesized electrochemically,[14,15] and chemically using a variety of oxidants, *e.g.*, $S_2O_8^{2-}$,[14,16] H_2O_2/HRP,[17] and a $S_2O_8^{2-}/Fe^{3+}$ dual oxidant system.[18] In this study, we show that in order to achieve a combination of high conductivity and bulk nanoscale morphology the experimental parameters must be carefully controlled. We also uncover a potentially new method to control nanoscale morphology by leveraging freshly precipitated protonated monomer as a template/seed for polymerization.

Results and discussion

Chemical oxidative polymerization of 2,5-dimethoxyaniline in aqueous 1.0M HCl using NaCl/H_2O_2 at −5 °C - 0 °C yields poly(2,5-dimethoxyaniline) hydrochloride, a dark green powder having room temperature DC conductivity $\sigma \sim 10^{-1}$ S cm^{-1}. Upon suction filtration in air the polymer forms a porous and lightweight mat on the filter funnel that can be lifted manually and cut with scissors. Fig. 1 shows that the powder has considerable nanostructure. In contrast, the analogous polymer obtained using $S_2O_8^{2-}$ does not form a compact mat on the filter funnel upon filtration and has granular morphology (Fig. 2). Importantly, it also has a lower conductivity (10^{-3}-10^{-2} S cm^{-1}). It is to be noted that the nanoscale morphology observed in the NaCl/H_2O_2 system is different from the classical nanofibrillar

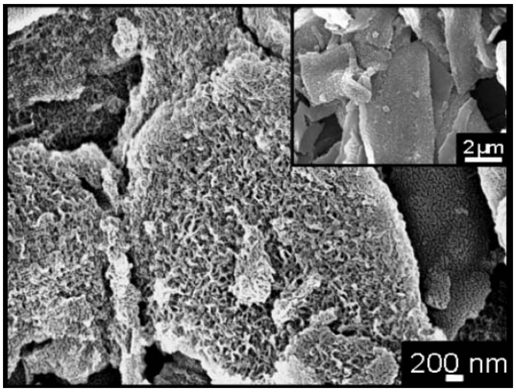

Fig. 1 SEM images of conducting chloride doped poly(2,5-dimethoxyaniline) using NaCl/H_2O_2. Inset: lower magnification image.

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[a]Department of Chemical Engineering, University of Massachusetts Lowell, Lowell, MA, 01854, USA. E-mail: sanjeev_manohar@uml.edu; Fax: +1-978-934-3047; Tel: +1-978-934-3162
[b]Department of Chemistry, University of Massachusetts Lowell, Lowell, MA, 01854, USA
[c]Toxics Use Reduction Institute, University of Massachusetts Lowell, Lowell, MA, 01854, USA

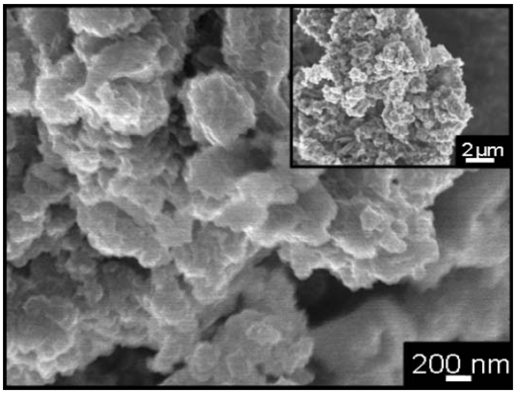

Fig. 2 SEM images of conducting chloride doped poly(2,5-dimethoxyaniline) using $S_2O_8^{2-}$ oxidant. Inset: lower magnification image.

morphology observed in the parent polyaniline system (see below).[2]

The redox potentials of poly(2,5-dimethoxyaniline) hydrochloride synthesized using the NaCl/H_2O_2 and $S_2O_8^{2-}$ are 0.25V and 0.35V (*vs.* SCE) respectively, suggesting that the lower conductivity of the latter may be due to over-oxidation of the polymer backbone. This is consistent with solution UV/Vis spectra of the corresponding base forms shown in Fig. 3, *e.g.*, the excitonic transition of the polymer synthesized using $S_2O_8^{2-}$ is at a higher energy (594 nm, 2.09 eV) compared to NaCl/H_2O_2 (609 nm, 2.04 eV). FT-IR spectrum (ATR) also shows a stronger ~1600 cm^{-1} (quinoidal) peak in the polymer obtained using $S_2O_8^{2-}$ although the striking similarity between the 2 spectra (Fig. 4) shows that coupling of monomer units has occurred predominantly in the preferred head-tail fashion. The ^{1}H NMR spectrum in CD_2Cl_2 (Fig. 5) shows a ~3 : 1 peak integration ratio for aliphatic/aromatic protons which is consistent with head-tail coupling of monomer units with 2 methoxy groups for each aromatic ring.

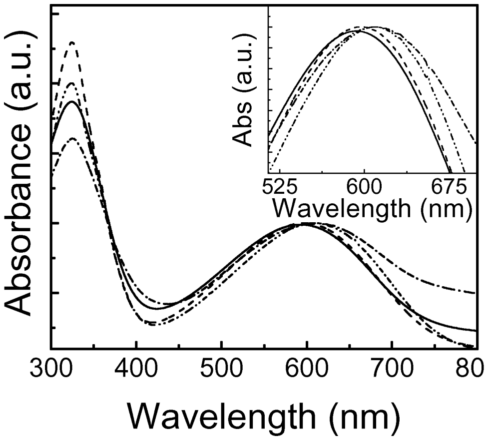

Fig. 3 Electronic absorption spectra (UV/vis) of poly(2,5-dimethoxyaniline) base synthesized using $S_2O_8^{2-}$ in NMP (solid line) and $CHCl_3$ (dash) and using NaCl/H_2O_2 in NMP (dash-dot) and $CHCl_3$ (dash-dot-dot). Inset: Expanded region.

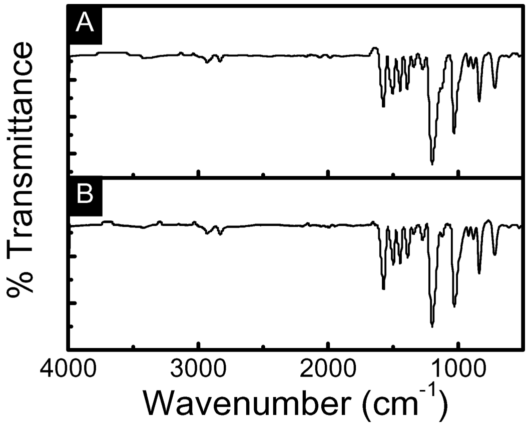

Fig. 4 Vibrational spectra (ATR-FT/IR) of poly(2,5-dimethoxyaniline) base synthesized using: (A) NaCl/H_2O_2, and (B) $S_2O_8^{2-}$.

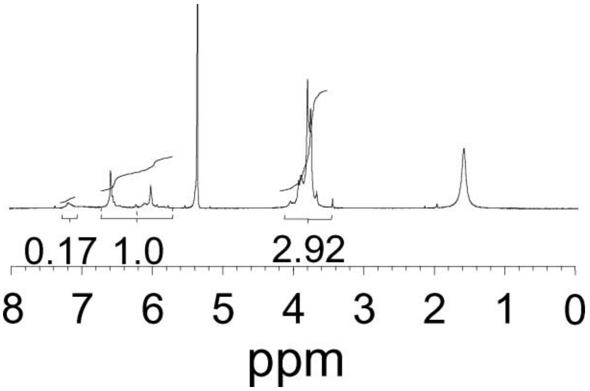

Fig. 5 ^{1}H NMR spectrum of poly(2,5-dimethoxyaniline) base synthesized using NaCl/H_2O_2 in CD_2Cl_2.

Highly conducting nanostructured poly(2,5-dimethoxyaniline) powder is obtained only under specific reaction conditions, e.g, a simple extension of our recently reported method for parent polyaniline nanofibers using H_2O_2 (satd. NaCl, 21 °C) yielded an insulating brown powder. When the reaction is carried out at −5 °C–0 °C a dark green powder having granular morphology and low conductivity (~10^{-3} S cm^{-1}) is obtained (no nanostructure). We carried out a series of reactions at 21 °C and at low temperature (−5 °C–0 °C) by gradually varying the amount of NaCl. At 21 °C a brown insulating powder is formed regardless of the NaCl concentration. At low temperature (−5 °C–0 °C) a dark green powder is formed at all NaCl concentrations, although the conductivity decreases monotonically to ~10^{-4} S cm^{-1} as a function of reaction time. A high value of 10^{-2} S cm^{-1} is observed if the reaction is not allowed to proceed >4h.

When the molarity of NaCl is reduced from 5.12M (15g/50 ml) to 1.71M (5g/50ml) we observed a curious phenomenon. The precipitated polymer held together in the form of a mat when the reaction mixture was filtered in air using a buchner filter funnel. The film is mechanically robust and can be easily removed manually and cut with scissors. This is very similar to our previous report on a highly conducting polypyrrole nanofiber film that could also be manually lifted from a filter funnel (granular polypyrrole could not be handled similarly).[19] Expectedly, the poly(2,5-dimethoxyaniline) powder shows considerable nanostructure having a conductivity ~10^{-2} S cm^{-1}. When the NaCl concentration is reduced to 1.53M (4.5g/50ml), the polymer precipitate has a higher conductivity, $\sigma_{RT} = 2.6 \times 10^{-1}$ S cm^{-1}, while still retaining a similar nanostructured morphology (Fig. 1). Upon further reduction of NaCl to 1.36M (4g/50ml) the conductivity decreases once again to ~10^{-2} S cm^{-1}. When the reaction is carried out in the absence of NaCl, the polymer precipitate has a lower conductivity (~10^{-3} S cm^{-1}) and no nanostructure.

As mentioned before the nanostructured morphology observed in chloride doped poly(2,5-dimethoxyaniline) powder (Fig. 1) is different from the non-woven spaghetti like nanofiber mesh that is commonly observed in parent polyaniline and other conducting polymer nanofibers synthesized by nanofiber seeding.[20-24] In fact, no nanostructure is observed when we attempted to seed the reaction with V_2O_5 nanofibers or with *N*,*N*-diphenyl-*p*-phenylenediamine (using H_2O_2 or $S_2O_8^{2-}$ oxidant)[25,26] suggesting that the evolution of nanostructure is triggered by a completely different mechanism. We noticed one important difference between aniline and 2,5-dimethoxyaniline in NaCl rich solutions as the temperature is reduced from 21 °C to 0 °C. Unlike anilinium hydrochloride which is completely soluble even at high NaCl concentrations, 2,5-dimethoxyanilinium hydrochloride is less soluble and begins to precipitate out as the temperature is lowered. Our working hypothesis is that this precipitate could be acting as seeds, or nucleation sites for initiation of polymerization and subsequent polymer growth. This is similar in principle to the template-free approach to polyaniline nanotubes using large organic dopant anions like naphthalenesulfonates.[27] The physical characteristics of this precipitate, such as shape, size, crystallinity, could be playing an important role in determining the bulk morphology of the final product. This would depend very much on the equilibrium reaction between unprotonated and protonated monomer species in solution. At high NaCl concentration the equilibrium is shifted in favor of salt formation resulting in significant precipitation of the monomer from solution which is consistent with a highly turbid, grey colored suspension observed when the NaCl concentration is high (5.12M). Since the monomer concentration in solution is very low, polymerization initiated by H_2O_2 on the surface of these large-sized precipitates would proceed non directionally towards the interior of the precipitate resulting in a compact, granular morphology as is experimentally found to be the case. In contrast, at low NaCl concentration, *i.e.*, in the 1.36M–1.71M range, 2,5-dimethoxyaniline will precipitate more gradually from solution resulting in a more loosely packed dispersion that is in dynamic equilibrium with monomer in solution. Initiation of polymerization on the surface of these loosely bound aggregates is expected to involve both precipitated monomer and monomer present is solution. We believe this would lead to an expanded, loosely packed polymer precipitate having a high surface area. Our working hypothesis is that unlike the parent polyaniline system classical nanofiber formation is suppressed in the 2,5-dimethoxyaniline system because polymerization takes place in the solid state on the surface of freshly precipitated 2,5-dimethoxyaniline hydrochloride salt. Indeed, when a solution of 2,5-dimethoxyanilinium hydrochloride at NaCl concentration in the 1.36M–1.71M range is cooled the suspension that is formed is visually very different from the high NaCl system and there is significantly less precipitate. Clearly, additional studies are required to confirm the above hypothesis.

Evidence consistent with the above hypothesis was obtained from charge/discharge studies, *i.e.*, the fluffy, nanostructured precipitate of poly(2,5-dimethoxyaniline) synthesized using $NaCl/H_2O_2$ shows superior charge storage capacity compared to the corresponding granular polymer synthesized using $S_2O_8^{2-}$. An accurately weighed amount of polymer was sandwiched between a folded Pt foil subjected to potential cycling between 0.0V and 0.5V for 50 cycles without significant loss of electroactivity. The specific capacitance was calculated using previously established methodology[28] and found to be 205 F g^{-1} for polymer synthesized using $NaCl/H_2O_2$ and 140 F g^{-1} for polymer synthesized using $S_2O_8^{2-}$ (Fig. 6). The results are consistent with nanostructured poly(2,5-dimethoxyaniline) having a higher surface area compared to granules. The high available surface area increases contact with electrolyte ions in solution that improves capacitive charge storage by permitting more redox sites to participate in the charge/discharge process. For example, in the parent polyaniline system large capacitive charge storage values are reported in polyaniline nanowires also having a high surface area (Langmuir, or BET).[29]

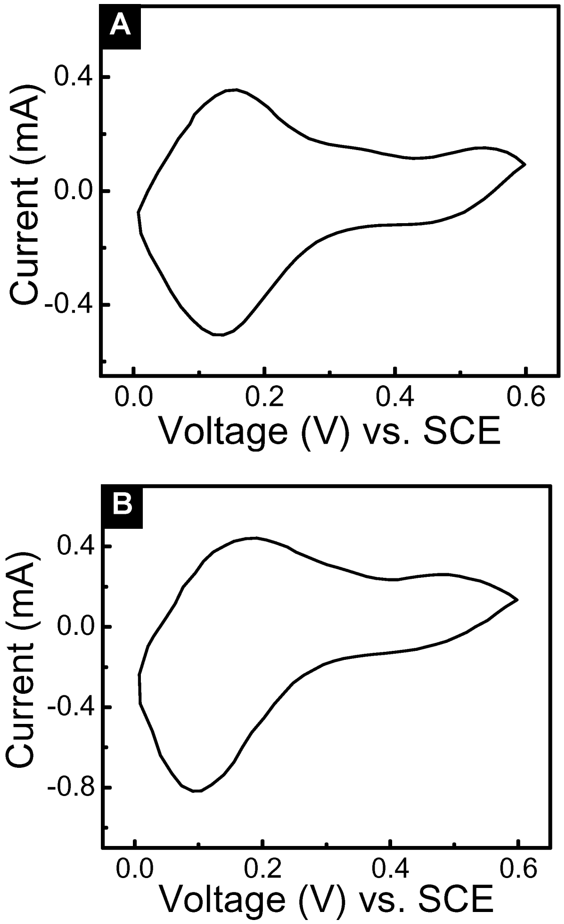

Fig. 6 Cyclic voltammograms of chloride doped poly(2,5-dimethoxyaniline) in 1M HCl, (A) synthesized using $NaCl/H_2O_2$, (B) synthesized using $S_2O_8^{2-}$. Pt working/counter electrodes, SCE reference.

The higher conductivity (~10^{-1} S cm^{-1}) of the polymer synthesized using $NaCl/H_2O_2$ (*vs.* $S_2O_8^{2-}$) can be rationalized not only on the basis of fewer chain defects (overoxidation/degradation), but also because of more homogeneous polymerization and doping of the loosely bound monomer precipitate. We believe this early precipitate would have good surface contact with H_2O_2 and dopant ions resulting in a cleaner polymerization/doping process. In contrast, at high NaCl concentration the monomer precipitates almost completely out of solution which could result in inhomogeneous polymerization and doping levels, *e.g.* surface polymerization and doping. One of the main reasons for using added NaCl in the reaction was to disfavor radical pathways and to direct the reaction along the preferred ionic pathway. The effect of added NaCl is an interplay between suppression of free radical pathways (preferred) and precipitation of the monomer completely from solution (not preferred). The optimum NaCl concentration is one which is high enough to suppress free-radical reaction pathways and yet low enough to maintain a significant amount of monomer in solution. This delicate balance must be further refined in order to promote the bulk nanostructure formation. This is one of the reasons why the successful use of $NaCl/H_2O_2$ as an oxidizing system depends so much on the nature of the ring-substituent, *i.e.*, where key precipitation parameters, such as amine pK_a, solubility, precipitation rate, crystallinity, *etc.*, are all system specific. The nanoscale morphology of poly(2,5-dimethoxyaniline) synthesized using $NaCl/H_2O_2$ is most probably not a key factor in the higher bulk conductivity. This is consistent with previously published studies on parent polyaniline nanofibers where no increase in conductivity is observed, and also because conductivity values are usually measured as a pressed pellet, *i.e.*, any nanostructure would be destroyed in the pellet press.

It is instructive to compare the 2-methoxy- and 2,5-dimethoxyaniline systems to illustrate the relative importance of early precipitate formation and the accessibility of the 5-position of the aromatic ring. When NaCl is added to a solution of 2-methoxyaniline in aq. 1.0M HCl, a light yellow precipitate of the corresponding hydrochloride salt is observed. However, even after >6h exposure to $NaCl/H_2O_2$, the reaction yields a dark-brown insulating solid regardless of salt concentration. This suggests that the open 5-position is playing an important role in disfavoring classical head-tail coupling on monomer units, possibly by coupling with hydroxy radicals to yield 2-methoxy-5-hydroxy units that would readily hydrolyze to *p*-benzoquinones. That this does not take place when $S_2O_8^{2-}$ is used, *i.e.*, linear head-tail coupling is observed, underscores the myriad of free-radical pathways that are favored in H_2O_2 systems.

Lastly, there are important spectroscopic differences in solution and the solid state between mono-substituted and di-substituted polyanilines. For example, we have recently shown that emeraldine base solutions of poly(2-methylaniline) in organic solvents display pronounced solvatochromism, *i.e.*, have different colors in different solvents ($\Delta\lambda_{max}$ ~62 nm).[30,31] Other derivatives, such as 2-ethyl, 2-methoxy, and 2-ethoxyanilines also display solvatochromism that is driven by a change in chain conformation in solution. Dipolar aprotic solvents like NMP promote an extended rod-like conformation resulting in lower transition energies of the excitonic peak centered ~2 eV. Solvents like $CHCl_3$, CH_2Cl_2, *etc.*, promote a more coil-like chain conformation resulting in higher transition energies. In contrast, the excitonic peak in poly(2,5-dimethoxyaniline) does not display solvatochromism (NMP: λ_{max} = 609 nm; $CHCl_3$: λ_{max} = 610 nm). It is not clear why this is the case, although we rationalize it on the basis of solvation induced steric effects, *i.e.*, energy barriers to conformational changes in solution as a result of equal solvation of both methoxy groups. Specific polarity scales such as the Taft's β-scale and donor number (DN) that play a significant role in the evolution of solvatochromic phenomena in 2-substituted derivatives[31] do not transition readily to symmetric 2,5-substituted systems.

Conclusions

In summary, we show for the first time: (i) a milder, green chemistry method to synthesize poly(2,5-dimethoxyaniline) using $NaCl/H_2O_2$ without any added transition metals, enzymes, or polymeric dopants, (ii) synthesis of highly conducting poly(2,5-dimethoxyaniline) powder having significant nanoscale morphology, (iii) enhanced charge storage capacity in as-synthesized nanostructured poly(2,5-dimethoxyaniline), and (iv) tailoring the ionic strength of the system to induce the formation of a high surface area monomer precipitate that promotes bulk nanoscale morphology.

Experimental

Materials

2,5-Dimethoxyaniline (98%), ammonium peroxydisulfate (98%), sodium chloride, hydrogen peroxide, were purchased from Sigma-Aldrich (Milwaukee, WI). Concentrated hydrochloric acid (37%), *N*-methyl-2-pyrrolidinone (NMP, 99+%), chloroform (99+%), dichloromethane (DCM, 99+%), concentrated ammonium hydroxide (35%) were purchased from Acros Organics USA (Morris Plain, NJ). Acetonitrile, acetone (99+ %) were purchased from Pharmaco-AAPER. All chemicals were used without further purification.

Synthesis procedure

Nanostructured poly(2,5-dimethoxyaniline) powder is synthesized by oxidative polymerization of 2,5-dimethoxyaniline in an aq. acidic system using H_2O_2 oxidant. The potential of the reaction is monitored continuously with time (Pt electrode, SCE reference).[2] In a typical procedure, NaCl (4.5 g) is slowly added to a solution of 2,5-dimethoxyaniline (2 g) dissolved in 50 ml aq. 1M HCl until the monomer begins to precipitate. The reaction mixture is kept in an ice bath with stirring and the temperature of the reaction is continuously monitored. 5 mL of 35 wt% H_2O_2 is added to the reaction mixture at ~−5 °C and the reaction mixture is stirred for 3 h with the temperature maintained between 0 and −5 °C. The reaction mixture is then vacuum filtered, washed with copious amounts of 1M HCl and acetonitrile to remove the unreacted monomer, oligomers and salt. The product obtained is dried in a vacuum oven at 50 °C for 12 h. The yield of the poly(2,5-dimethoxyaniline) emeraldine salt obtained is 300 mg. For spectroscopic characterization, emeraldine salt is converted to a processable emeraldine base by stirring the emeraldine salt in 500 ml 0.1M NH_4OH for 12 h followed by vacuum filtration, washings with D.I. H_2O (500 ml) and acetonitrile (100 ml) and drying in a vacuum oven for 12 h at 30 °C. Chemical synthesis of poly(2,5-dimethoxyaniline) using $(NH_4)_2S_2O_8$ oxidant is carried out at 0 °C by adding 0.75 g of $(NH_4)_2S_2O_8$ to a solution of 2 g 2,5-dimethoxyaniline in 50 ml 1M HCl (monomer/oxidant ratio 4 : 1). The potential of the reaction is monitored continuously with time. After 30 min, the product is filtered and the product is purified and characterized similar to that synthesized using H_2O_2 oxidant.

Characterization

Four-probe pressed pellet conductivity measurements on chloride doped poly(2,5-dimethoxyaniline) was carried out using the standard van-der Pauw method. Electronic absorption spectra (UV/vis) of solutions of poly(2,5-dimethoxyaniline) base in NMP and $CHCl_3$ (0.1mg/5ml) were obtained using an Agilent 8453 spectrophotometer. Attenuated total reflectance ATR/FTIR spectra were recorded on an AVATAR 360 FTIR using a dried sample of poly(2,5-dimethoxyaniline) base. Electrochemical measurements were recorded at room temperature on an Arbin electrochemical workstation (Model # MSTAT4+, serial # DEMO-14). For potential time profile measurements, a platinum wire immersed in the reaction media was used as a working electrode, another platinum wire was used as a counter electrode and saturated calomel electrode (SCE) was used as the reference electrode. For capacitive charge storage measurements using cyclic voltammetry 1 mg of freshly synthesized chloride doped poly(2,5-dimethoxyaniline) was placed on a platinum mesh working electrode and the potential cycled in the range 0.0-0.5 V for 50 cycles at a scan rate of 20 mV s^{-1}. The experimental approach including equations used to calculate the specific capacitance are similar to analogous studies on parent polyaniline nanofibers.[28] ^1H NMR spectroscopy was carried out on a Bruker 500 MHz spectrometer in deuterated dichloromethane (CD_2Cl_2). Polymer morphology was imaged using a JEOL JSM-1401F FE-SEM with a field emission gun operated at 5 keV. To acquire images, the sample was placed on the carbon tab sample holder and coated with Au using a Denton Vacuum Desk II sputter coater.

Acknowledgements

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