Chemical synthesis of PEDOT nanofibers†

Xinyu Zhang, Alan G. MacDiarmid and Sanjeev K. Manohar*

Received (in Cambridge, UK) 8th August 2005, Accepted 31st August 2005
First published as an Advance Article on the web 26th September 2005
DOI: 10.1039/b511290g

A one-step, room-temperature method is described to chemically synthesize bulk quantities of microns long, 100–180 nm diameter nanofibers of electrically conducting poly(3,4-ethylenedioxythiophene) (PEDOT) in the form of powders, or as optically transparent, substrate-supported films using a V_2O_5 seeding approach.

The poly(3,4-ethylenedioxythiophene) (PEDOT) family of polymers is a technologically important class of conducting polymers displaying high stability, moderate band gap, low redox potential and high optical transparency in its electrically conductive state.[1] Its inherent insolubility in common solvents has been successfully circumvented by using water-dispersible polymeric sulfonic acids such as poly(styrenesulfonic acid) (PSS), during its chemical synthesis that result in stable dark-blue aqueous dispersions of PEDOT·PSS that are now commercially available and used in antistatic coatings, electrode materials, *etc.*[1] Films can be obtained by *in situ* adsorption polymerization on glass, plastics,[2] and fabrics.[3] Recently, highly conducting films ($\sim$900 S cm^{-1}) have been obtained by spin coating PEDOT and its ring-substituted derivatives on a glass surface.[4] Powders and films of PEDOT obtained so far have granular or particulate morphology which has seriously limited studies on 1D transport in these systems. While PEDOT nanotubes have been synthesized electrochemically in the pores of Al_2O_3 template,[5] we believe significant opportunities exist in developing a convenient chemical synthetic route to the bulk synthesis of nanostructured PEDOT powders and films for potential use in the design of next-generation nanoelectronic circuits and field-emission devices.[5,6] Chemical approaches that have successfully yielded nanofibers of polyaniline[7] and polypyrrole[8] yield only granular powder in the PEDOT system.

In this study, we describe a one-step, room-temperature method to chemically synthesize bulk quantities of microns long, 100–180 nm diameter nanofibers of electrically conductive PEDOT in the form of powders, or as optically transparent, substrate-supported films using a V_2O_5 seeding approach. This method is a variant of our recently reported synthesis of polypyrrole nanofibers using V_2O_5 nanofibers as sacrificial seeds during the chemical synthesis of polypyrrole in aq. 1.0 M HCl,[8] where the V_2O_5 nanofibers: (i) rapidly initiate fibrillar polymer growth, and (ii) slowly dissolve in aq. 1.0 M HCl eliminating cumbersome template removal steps. The V_2O_5 sacrificial seeds must survive long enough to initiate fibrillar polymer growth, *i.e.*, the polymerization rate should be faster than the rate of dissolution of V_2O_5 seeds. A direct application of this method to the PEDOT system, however, yields only granular powders. This is due to a combination of low solubility of EDOT in aqueous mineral acids (oily droplets observed) and dissolution of V_2O_5 seeds before onset of polymerization.

These two issues are circumvented by using organic acids instead of mineral acids. Several organic acids were tested and aq. 1.0 M DL-camphorsulfonic acid (CSA) was found to be optimum. In aq. 1.0 M CSA, V_2O_5 nanofibers dissolve more slowly, and the EDOT monomer dissolves completely resulting in a homogeneous reaction mixture. Polymerization of EDOT in aq. 1.0 M CSA using $(NH_4)_2S_2O_8$ oxidant in the presence of V_2O_5 nanofibers seeds (15–20 nm diameter) results in a dramatic change in the bulk morphology of the PEDOT precipitate from granular to nanofibrillar (Fig. 1). The unseeded control reaction yielded only PEDOT powders having granular morphology. The V_2O_5 nanofibers are not polymerization templates in the conventional sense, but are seeds that help orchestrate a change in morphology, *e.g.*, $\sim$3 mg of V_2O_5 nanofibers are sufficient to affect a bulk change in morphology from granular to nanofibrillar in $\sim$600 mg of the PEDOT precipitate. The synthesis is extremely simple and carried out in air at room temperature, and the product can be isolated by simply filtering the reaction mixture and washing the precipitate with aq. HCl. The scanning electron microscopy (SEM) image of PEDOT powder obtained by V_2O_5-seeding shows a near quantitative (>95%) amount of nanofibers even at low magnification. The PEDOT nanofibers are in the form of a non-woven mesh, 3–10 microns long and 100–180 nm in diameter, exhibiting a pressed pellet conductivity $\sigma_{RT} = 16$ S cm^{-1}. After washing with aq. 1.0 M HCl, the PEDOT powder has elemental analysis; C, 45.57; H, 3.34; S, 20.14; O, 27.46; Cl, 3.47; total, 99.98%, which is consistent with the empirical formula $(PEDOT)(CSA)_{0.11}(HSO_4)_{0.12}(Cl)_{0.11}(H_2O)_{0.19}$ and a doping level of 34%. The HSO_4^- and Cl^- dopant ions result from the $(NH_4)_2S_2O_8$ oxidant

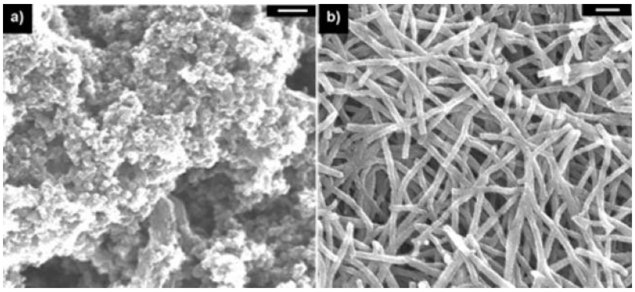

Fig. 1 Scanning electron microscopy (SEM) images of PEDOT powder synthesized: (a) without added V_2O_5 seeds (control); (b) with added V_2O_5 seeds. Scale: 500 nm.

Alan G. MacDiarmid Center for Innovation, Department of Chemistry, The University of Texas at Dallas, Richardson, TX 75080, USA. E-mail: sanjeev.manohar@utdallas.edu; Fax: 972-883-6586; Tel: 972-883-6536

† Electronic supplementary information (ESI) available: Synthesis of PEDOT nanofibers. See http://dx.doi.org/10.1039/b511290g

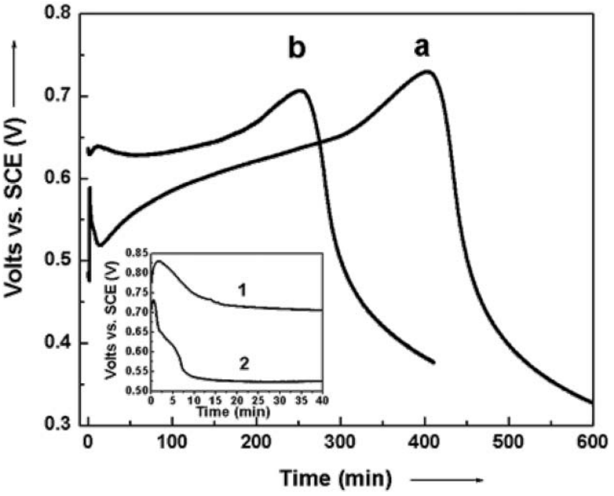

Fig. 2 Potential–time profiles of polymerization of EDOT in aq. 1.0 M CSA: (a) without added V_2O_5 seeds (control) and (b) with added V_2O_5 seeds. Inset: potential–time profiles of V_2O_5 seeds in (1) aq. 1.0 M CSA and (2) aq. 1.0 M HCl.

and the aq. 1.0 M HCl used to wash the precipitate to dissolve any residual V_2O_5 seeds eliminating thereby, the need for special post-synthesis V_2O_5 removal steps. The yield is ~95% based on $(NH_4)_2S_2O_8$.

Both large organic dopant anions and fibrillar seeds are necessary for quantitative nanofiber formation in the PEDOT system unlike the polyaniline system where either would suffice, *e.g.*, polyaniline nanofibers/tubes can be obtained under unseeded conditions when large organic dopant anions are used,[9] and also under seeded conditions in the absence of large organic dopant anions.[7] In the PEDOT system, both large organic anions and nanofibrillar seeds are important in optimizing synthetic conditions that favor nanofiber formation, *e.g.*, improving EDOT solubility, increasing the rate of polymerization, and decreasing the rate of dissolution of the V_2O_5 nanofibers. Potential-time profiling[10] of the polymerization provides evidence consistent with this rationale (Fig. 2). The duration of the potential increase is generally associated with the presence of $(NH_4)_2S_2O_8$ in the reaction mixture and active formation of polymer chains, while the potential fall is associated with the depletion of $(NH_4)_2S_2O_8$ and the cessation of chain growth.[10] The initial potential is higher in the seeded system compared to the unseeded system (0.62 *vs.* 0.55 V) consistent with the oxidizing nature of V_2O_5, and with the navy blue color that is formed even prior to addition of $(NH_4)_2S_2O_8$. Polymerization is also faster in the seeded system with the onset of the potential drop occurring in 4 h compared to 6.5 h for the unseeded system suggesting that V_2O_5 nanofiber seeds are catalyzing the polymerization. The inset in Fig. 2 describes the potential-time profile of the dissolution of pure V_2O_5 nanofibers in CSA *vs.* HCl (no monomer or oxidant). From the initial slope of the two plots, it is clear that V_2O_5 nanofibers dissolve more slowly in aq. 1.0 M CSA compared to aq. 1.0 M HCl allowing sufficient time for the V_2O_5 nanofibers to orchestrate fibrillar polymer growth.

During the polymerization, and in the duration associated with the rise in potential values in Fig. 2, light-blue colored films of PEDOT deposit spontaneously on the walls of the reaction vessel and any inert substrate such as PET. This is similar to corresponding films observed on PET in the polyaniline and polypyrrole seeded systems.[7,8] These PEDOT films also have nanofibrillar morphology and are present in the form of a densely packed non-woven mat having length scales similar to the bulk precipitate (Fig. 3(a)). They are strongly adhering to the PET surface and pass a rough Scotch tape test. These films can also be obtained in any desired pattern on the PET surface using the Line Patterning method[2] and we have constructed flexible and optically transparent prototype electronic devices such as field-effect transistors and sensors. These films (150–175 nm thick, $R = 4.3\ \mathrm{k\Omega}\ \square^{-1}$) are more optically transparent (83 *vs.* 76%) and more conducting (4.3 *vs.* 7.2 $\mathrm{k\Omega}\ \square^{-1}$) than those obtained by spin/dip coating,[2] and less optically transparent (83 *vs.* 87%) and less conducting (4.3 *vs.* 1.5 $\mathrm{k\Omega}\ \square^{-1}$) than commercial PEDOT·PSS/PET films (Fig. 3(b)).[11] However, we expect the conductivity of our as-synthesized PEDOT/PET films to increase in the presence of secondary dopants such as ethylene glycol and imidazole and by using our seeding approach to the recently reported highly conducting ring-substituted derivatives of PEDOT.[4]

In summary, we describe for the first time: (i) a rapid and convenient room-temperature chemical method to synthesize bulk quantities of PEDOT nanofibers under aqueous conditions, (ii) the

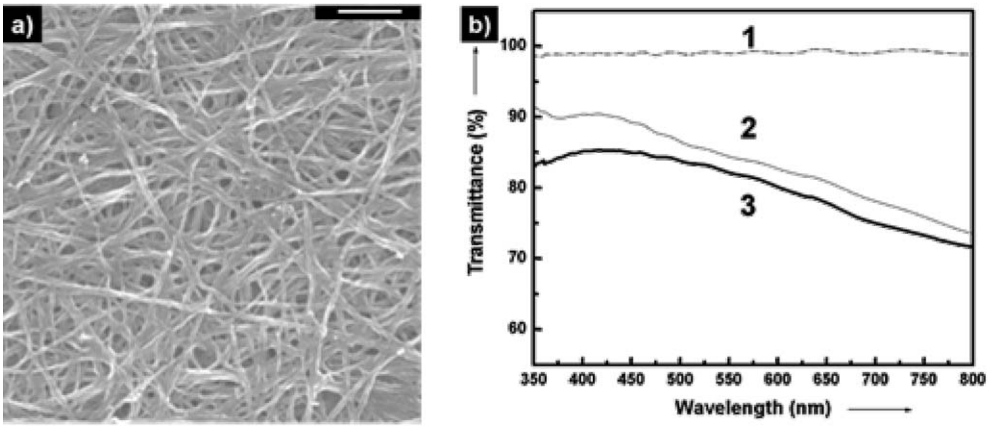

Fig. 3 (a) Scanning electron microscopy (SEM) image of an *in situ* deposited film of PEDOT on PET substrate. Scale: 500 nm. (b) Electronic absorbance spectra of (1) PET control, (2) commercial conducting coating of PEDOT on PET (Orgacon EL 1500) and (3) *in situ* deposited film of PEDOT nanofibers on PET.

use of a combination of organic acids and V_2O_5 nanofiber seed templates to alter the morphological trajectory of the PEDOT system which is intrinsically recalcitrant to fibrillar polymer growth, and (iii) the synthesis of strongly adherent, electrically conducting films of nanofibers of PEDOT having high optical transparency directly from the polymerization mixture.

We gratefully acknowledge technical assistance from Mr Sumedh Surwade and financial support from The University of Texas at Dallas.

Notes and references

1 L. B. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J. R. Reynolds, *Adv. Mater.*, 2000, **12**, 481; L. B. Groenendaal, G. Zotti, P.-H. Aubert, S. M. Waybright and J. R. Reynolds, *Adv. Mater.*, 2003, **15**, 855; G. Heywang and F. Jonas, *Adv. Mater.*, 1992, **4**, 116; I. F. Perepichka, M. Besbes, E. Levillain, M. Salle and J. Roncali, *Chem. Mater.*, 2002, **14**, 449.

2 D. Hohnholz, H. Okuzaki and A. G. MacDiarmid, *Adv. Funct. Mater.*, 2005, **15**, 51.

3 K. H. Hong, K. W. Oh and T. J. Kang, *J. Appl. Polym. Sci.*, 2005, **97**, 1326.

4 Y.-H. Ha, N. Nikolov, S. K. Pollack, J. Mastrangelo, B. D. Martin and R. Shashidhar, *Adv. Funct. Mater.*, 2004, **14**, 615.

5 B. H. Kim, D. H. Park, J. Joo, S. G. Yu and S. H. Lee, *Synth. Met.*, 2005, **150**, 279.

6 J. L. Duvail, P. Retho, C. Godon, C. Marhic, G. Louarn, O. Chauvet, S. Cuenot, B. Nysten, L. Dauginet-DePra and S. Demoustier-Champagne, *Synth. Met.*, 2003, **135-136**, 329.

7 X. Zhang, W. J. Goux and S. K. Manohar, *J. Am. Chem. Soc.*, 2004, **126**, 4502.

8 X. Zhang and S. K. Manohar, *J. Am. Chem. Soc.*, 2004, **126**, 12714.

9 L. Zhang and M. Wan, *Thin Solid Films*, 2005, **477**, 24.

10 X.-G. Li, M.-R. Huang and Y.-M. Hua, *Macromolecules*, 2005, **38**, 4211; S. K. Manohar, A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, 1991, **41**, 711; Y. Wei, K. F. Hsueh and G. W. Jang, *Polymer*, 1994, **35**, 3572.

11 Orgacon EL 1500, Agfa-Gevaert Group: PEDOT coatings on PET.