Novel Poly(acrylic acid)-Mediated Formation of Composited, Poly(3,4-ethylenedioxythiophene)-Based Conducting Polymer Nanowires

Xuping Sun*,[†] and Matthias Hagner[‡]

Fachbereich Chemie and Fachbereich Physik,
Universität Konstanz, Universitätsstrasse 10,
D-78457 Konstanz, Germany

Received August 28, 2007
Revised Manuscript Received October 25, 2007

In recent years, conducting polymers have received considerable attention because of their combination of useful mechanical, optical, and electronic properties[1] and potential applications to electronic devices, sensors, corrosion protection, and actuators, etc.[2] The synthesis of conjugated polymers in a form that can be easily processed in aqueous medium has been one of the major challenges in the fields of conducting polymers and has stimulated much progress in the commercial arena.[3] Among them, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most promising conducting polymers and widely studied because it exhibits some very interesting properties including transparent in thin films, highly conductive, and more stable than most other conducting polymers.[4] PEDOT is usually prepared through chemical or electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) monomer. Unfortunately, the resulting PEDOT is an insoluble and therefore not processable polymer. The solubility problem was subsequently circumvented by using a water-soluble poly(styrene sulfonic acid) (PSS) as the charge-balancing dopant during polymerization, leading to water-soluble, submicrometer sized gel particles of PEDOT:PSS composite.[5] It is further evidenced that the coating of such PEDOT:PSS dispersion on the substrate only gives a polymer film with a granular morphology.[6]

Up to now, there are many papers reporting on the preparation of PEDOT nanostructures including nanoparticles and one-dimensional (1D) nanostructures. For example, PEDOT nanoparticles were prepared by dispersion polymerization of EDOT monomer in a methanol/water mixture in the presence of a stabilizer.[7] Nanostructured PEDOT polymers in the form of tubes, rods, thimbles, and belts were prepared by using Al_2O_3 membrane as a hard template.[8] Another method for the preparation of EDOT nanotubes is based on electrochemical deposition of PEDOT around the electrospun nanofibers templates of biodegradable poly(L-lactide) (PLLA) or poly(lactide-*co*-glycolide) (PLGA) and the following removing the fiber templates.[9] PEDOT nanorods were also successfully fabricated with a reverse cylindrical micelle-mediated interfacial polymerization technique.[10] Besides, PEDOT nanofibers were synthesized by using a V_2O_5 seeding approach.[11]

Nanocomposites are a special class of hybrid materials with versatile properties provoked by combining the merits of the sources and may find applications in many fields and therefore, the synthesis of such kind of materials has become the research focus.[12] However, the method for preparing water-dispersible, PEDOT-based nanocomposites with unique morphologies, to the best of our knowledge, is not available in the literature. In this communication, we develop a polyelectrolyte-based preparative route to composited nanowires based on PEDOT conducting polymer, involving chemical polymerization of EDOT monomer at elevated temperature for several hours or at room temperature for several days with the use of $FeCl_3$ as an oxidant in the presence of a poly(acrylic acid) (PAA). This polymerization process leads to water-dispersible, wirelike nanocomposites, namely, nanowires which are about 20 nm in diameter and several hundred nanometers in length and at the same time, exhibits excellent conductivity. It is found that such nanowires are assemblies consisting of smaller nanowires and the use of PAA in the synthesis solution is crucial to their formation. Nanocomposites in the form of flowers and cages can be obtained by simply varying the amount of PAA used. A possible mechanism is also proposed to explain the formation of the assemblies.

EDOT and PAA were purchased from Aldrich, and $FeCl_3$ was bought from Merck. All chemicals were used as received without further purification. Sample 1 was prepared as follows: In a typical experiment, 1 mL of 0.2 M EDOT in tetrahydrofuran was added into 0.009 M PAA H_2O/ethanol solution (H_2O:ethanol = 3:1, pH ≈ 6.95) with 1:1 molar ratio of PAA (repeating unit) to EDOT, then 0.8 mL of 1.6 M $FeCl_3$ aqueous solution was introduced, and the mix solution thus formed was heated at 80 °C for 4 h, leading to a green solution. As-obtained products were concentrated by centrifugating the solution and sequentially washed with water and ethanol several times to remove unused reactants and reaction byproducts, and then were dispersed again in water for further characterization.

Transmission electron microscopy (TEM) measurements were made on a Zeiss LIBRA 120 microscope operated at an accelerating voltage of 120 kV. Samples for TEM examination were made by placing a drop of the disersion on a carbon-coated copper grid and air-dried at room temperature. For characterization by scanning electron microscopy (SEM) 20 μL of the dispersion was placed on an indium tin oxide (ITO) glass slide and air-dried at room temperature. SEM measurements were made on a Zeiss CrossBeam 1540XB microscopy at an accelerating voltage of 5 kV.

Figure 1 shows typical TEM images of the resulting dispersion. Lower magnification TEM image (Figure 1a) indicates that the dispersion consists of a large quantity of nanowires. It is clearly seen that some nanowires are well-separated from each other, and at the same time, a fraction of nanowires seem to have sintered. However, a closer examination reveals that these nanowires are not in direct physical contact, which can be evidenced by higher magnification TEM image (Figure 1b). It should be noted that the evaporation of the solvent and the high vacuum used for sample preparation and characterization in the TEM technique may have led to secondary aggregation of these nanowires on the grid substrate.[13] From Figure 1b, it is also found that the nanowires are about 20 nm in diameter and several hundred nanometers in length. Interestingly, a closer view of one single nanowire reveals that it is an assemblied structure consisting of smaller nanowires in a side-by-side manner (inset in Figure 1b).

We analyzed the elemental composition of the nanowires after centrifugating them from the dispersion and drying them under vacuum overnight at 50 °C. On the basis of the elemental composition (C, 49.36; H, 3.14; O, 33.87; S, 13.25 (total: 99.64)), we can conclude that the nanowires formed from EDOT

---

* Correspondence should be addressed to this author. E-mail: sun.xuping@hotmail.com.
[†] Fachbereich Chemie, Universität Konstanz.
[‡] Fachbereich Physik, Universität Konstanz.

10.1021/ma701935j CCC: $37.00

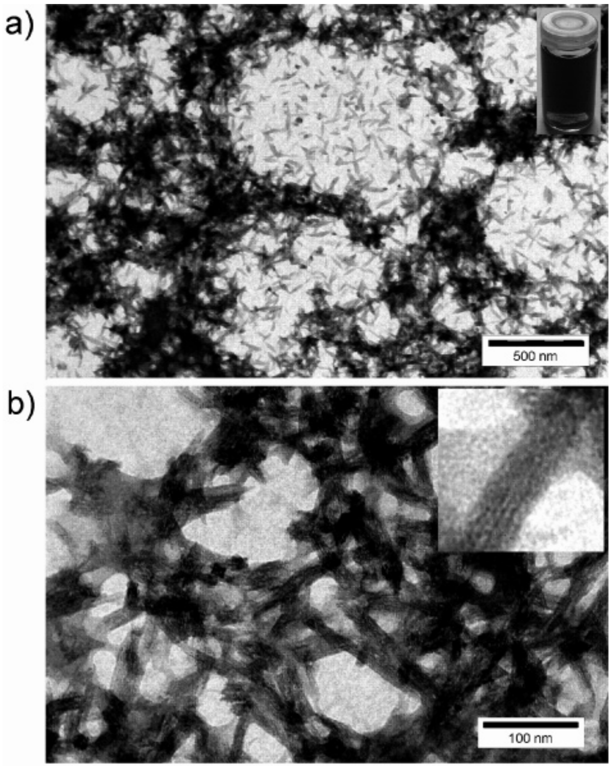

Figure 1. (a) Lower magnification TEM image of sample 1. Inset: the photograph of the solution. (b) Higher magnification TEM image of sample 1. Inset: a closer view of one single nanowire.

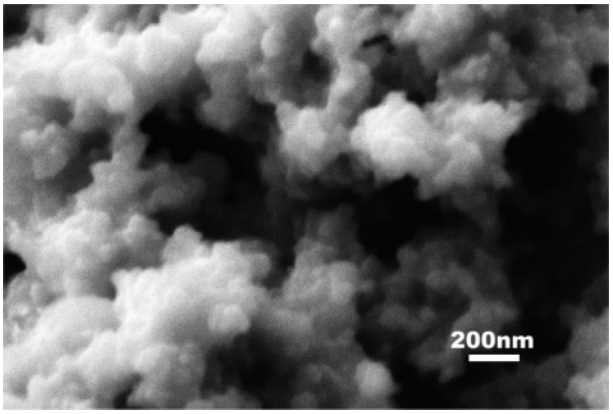

Figure 2. SEM image of PEDOT structures obtained in the absence of PAA.

and PAA and the chemical polymerization of EDOT by $FeCl_3$ in the presence of PAA results in the formation of PEDOT:PAA composites. We also measured the dc conductivity of nanowires dried under vacuum overnight at 50 °C with the standard four-probe technique and it suggests that their conductivity is high up to about 0.56 S/cm which is comparable to that of commercial available PEDOT:PSS complex.[4] Although the PEDOT:PSS dispersion in water is dark blue in color, the PEDOT:PAA dispersion in our present study is green in color (inset in Figure 1a), which may be due to the involvement of different polyelectrolyte and different morphology of the composited products obtained.

It should be noted that the use of PAA in the synthesis solution was critical to the formation of these nanowires, which can be evidenced by the fact that we only obtained irregular aggregated structures of small nanoparticles when the synthesis was performed in the absence of PAA, as shown in Figure 2.

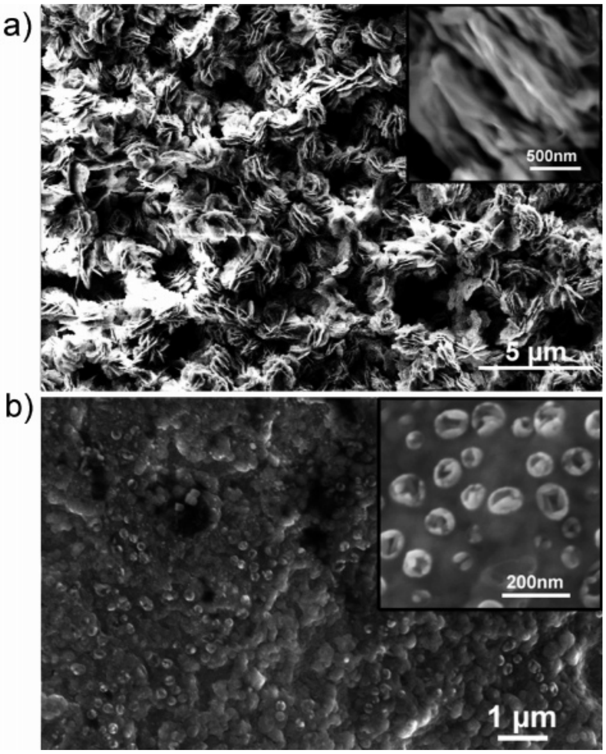

Figure 3. SEM image of the nanostructures obtained at molar ratio (a) 4:1 and (b) 1:10 of PAA (repeating unit) to EDOT, under otherwise identical conditions used for preparing sample 1. Inset: a closer view of the nanostructures.

To get further insight into the influence of the amount of PAA on the formation of the nanostructures, we prepared another two samples at different molar ratio of PAA to EDOT, under otherwise identical conditions used for preparing sample 1. Figure 3 shows typical SEM images of these two samples. When the molar ratio is increased up to 4:1, we obtained a large quantity of flower-like nanostructures, as shown in Figure 3a. A closer view of the flower (inset) reveals that each flower petal is also an assemblied structure consisting of small nanowires. However, when the molar ratio is decreased down to 1:10, most of the resulting nanostructures are cages in shape, as shown in Figure 3b. A closer view of such nanocage (inset) indicates that it consists of smaller nanoparticles.

The formation of these nanowires could be attributed to PAA-mediated self-assembly of PEDOT in solution. The possible formation mechanism is given as follows. When the reaction of chemical polymerization occurs, EDOT monomers are oxidized into positively charged oligomeric PEDOT chains first.[14] PAA is a kind of weak polyelectrolyte with partially negatively charged polymer chain and widely used as a building block for the creation of multilayer thin films on solid surfaces via a layer-by-layer technique based on electrostatic attraction interactions.[15] Liu et al. has demonstrated the use of PAA as a template for the generation of colloidal fibrils of polyaniline: PAA complex in solution through the electrostatic interactions between positively charged polyaniline and negatively charged PAA.[16] In our present study, it is expected that the electrostatic interactions between these positively charged PEDOT oligomers and the partially negatively charged PAA chain drive the oligomers to assembly along the PAA chain. Such PEDOT oligomers bound to the polymer chain then serve as “seeds” for the further polymerization of other EDOT monomers along the chain, that is, PAA chain acts as a “template” and PEDOT are polymerized along it. As a result, a PEDOT-coated PAA nanocomposite is formed. Although PAA chain is flexible in solution, the coating of PEDOT along it during the polymerization may change its nature of flexibility and a relatively rigid PEDOT-coated PAA 1D nanocomposite is formed. On the other hand, the PEDOT is rich in π-type bonds. It is well-known that $\pi-\pi$ interactions often exist in π-conjugated materials.[17] Li et al. has also demonstrated the self-assembly of gold nanoparticles into uniform spherical assemblies through $\pi-\pi$ interactions between the PEDOT capped on the individual nanoparticles.[18] We may suggest that the strong $\pi-\pi$ interactions between the PEDOT coated on the individual PAA chains can drive these smaller nanowires to further self-assembly into larger ones.[19] When there is no PAA in this synthesis, only PEDOT nanoparticles are formed first, and because of the absence of a effective "template" to direct their growth, it is not surprising to have found that only irregular aggregated structures are formed due to $\pi-\pi$ stacking interactions between these nanoparticles. When the molar ratio is 4:1, there are excessive PAA chains in the solution. There are two interactions including $\pi-\pi$ stacking between small nanowires and electrostatic attraction interactions between small naowires and excessive PAA chain involved in the assembly process. In this case, the assemblies of small nanowires formed can be further linked together by the excessive PAA chains leading to a hierarchical flower-like nanocomposite. When the molar ratio is 1:10, there are a large amount of excessive EDOT monomers in the solution and no enough PAA chains to template the polymerization of all of the EDOT monomers. When some monomers are polymerized along the PAA chains, the other monomers are polymerized simultaneously to form PEDOT nanoparticles. As-formed nanoparticles are driven to assembly along the PEDOT-coated PAA chains through $\pi-\pi$ interactions and on the other hand, they themselves are driven to self-assembly into larger particles due to the $\pi-\pi$ interactions between them. However, when the nanoparticles are coming closer to each other, they are pulled back to some extent by PEDOT-coated PAA chains which are simultaneously pulled ahead by nanoparticles. As a result, the nanoparticles fail to assembly into a closed particle and the PEDOT-coated PAA chains are forced to bend into cagelike nanocomposites. However, the detailed mechanism for the nanowire formation is not clear at present time and needs further investigation. It is worth while mentioning that when a positively charged polyelectrolyte is used, we failed to obtain nanocomposites with unique morphologies, which can be attributed to that the electrostatic repulsion interactions between the polyelectrolyte and PEDOT make it impossible for the polyelectrolyte chains to act as templates during the polymerization process. These observations further support that PAA severs as a template for the formation of these unique structures in our presence study.

In conclusion, the chemical polymerization of EDOT in the presence of PAA is proven to be an effective method for the preparation of green, water-dispersible PEDOT:PAA composites. It is found that these composites are nanowires assemblied from smaller nanowires in a side-by-side manner and exhibit excellent conductivity. It also suggests that the use of PAA in the synthesis solution plays a key role in the formation of nanowires and the morphologies of the nanocomposites can be controlled by varying the amount of PAA used. Our observations are significant for the following reasons: (1) It provides us a new water-dispersible and easily processable PEDOT dispersions for applications.[3,4] (2) It presents a simple self-assembly strategy for the morphology-controlled preparation of nanocomposites based on PEDOT. (3) It extends the use of polyelectrolyte as a template for designing interesting nanostructures.

Acknowledgment. X.S. thanks Prof. S. Mecking for being the research host and also appreciates the support from the Alexander von Humboldt Foundation. Dr. M. Krumova is appreciated for TEM characterization.

References and Notes

(1) Hulvat, J. F.; Stupp, S. I. *Adv. Mater.* **2004**, *16*, 589.
(2) (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (b) Hagleitner, C.; Hierlemann, A.; Lange, D.; Kummer, A.; Kerness, N.; Brand, O.; Baltes, H. *Nature (London)* **2001**, *414*, 293. (c) Wessling, B. *Adv. Mater.* **1994**, *6*, 226. (e) Smela, E. *Adv. Mater.* **2003**, *15*, 481.
(3) Cutler, C. A.; Bouguettaya, M.; Kang, T.-S.; Reynolds, J. R. *Macromolecules* **2005**, *38*, 3068.
(4) Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.
(5) (a) Bayer, A. G. Eur. Patent 440957, 1991. (b) Gevaert, A. Eur. Patent 564911, 1993.
(6) Xu, X.; Register, R. A.; Forrest, S. R. *Appl. Phys. Lett.* **2006**, *89*, 142109.
(7) Mumtaz, M.; Cuendias, A. de.; Putaux, J.-L.; Cloutet, E.; Cramail, H. *Maromol. Rapid Commun.* **2006**, *27*, 1446.
(8) (a) Kim, B. H.; Park, D. H.; Joo, J.; Yu, S. G.; Lee, S. H. *Synth. Met.* **2005**, *150*, 279. (b) Han, M. G.; Foulger, S. H. *Chem. Commun.* **2005**, 1.
(9) Abidian, M. R.; Kim, D.-H.; Martin, D. C. *Adv. Mater.* **2006**, *18*, 405.
(10) Jang, J.; Chang, M.; Yoon, H. *Adv. Mater.* **2005**, *17*, 1616.
(11) Zhang, X.; MacDiarmid, A. G.; Manohar, S. K. *Chem. Commun.* **2005**, 5328.
(12) Gangopadhyay, R.; De, A. *Chem. Mater.* **2000**, *12*, 608.
(13) Sun, X.; Jiang, X.; Dong, S.; Wang, E. *Macromol. Rapid Commun.* **2003**, *24*, 1024.
(14) Smith, R. R.; Smith, A. P.; Stricker, J. T.; Taylor, B. E.; Durstock, M. F. *Macromolecules* **2006**, *39*, 6071.
(15) (a) Decher, G. *Science* **1997**, *277*, 1232. (b) Caruso, F.; Caruso, R. A.; Mohwald, H. *Science* **1998**, *282*, 1111.
(16) Liu, J.-M.; Yang, S. C. *Chem. Commun.* **1991**, 1529.
(17) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491.
(18) Li, X.; Li, Y.; Tan, Y.; Yang, C.; Li, Y. *J. Phys. Chem. B* **2004**, *108*, 5192.
(19) (a) Sun, X.; Dong, S.; Wang, E. *Macromol. Rapid Commun.* **2005**, *26*, 1504. (b) Sun, X.; Hagner, M. *Langmuir* **2007**, *23*, 10441. (c) Schenning, A. P. H. J.; Meijer, E. W. *Chem. Commun.* **2005**, 3245.

MA701935J