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Direct dispersion of SWNTs in highly conductive solvent-enhanced PEDOT:PSS films

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Abstract Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is shown to be an effective dispersant for single-wall carbon nanotubes (SWNTs), enabling uniform aqueous suspensions to be obtained at weight loadings of up to 0.23 mg/ml (>1% by weight relative to PEDOT:PSS) without recourse to additional surfactants. Thin films spin-coated from PEDOT:PSS/SWNT suspensions exhibited sheet resistances of 90 Ω/sq. at 80 % transmittance, slightly higher than equivalent films of pure PEDOT:PSS which exhibited sheet resistances of 70 Ω/sq. at the same transmittance.

Keywords PEDOT:PSS, single walled carbon nanotube, transparent conducting film, nanocomposite, dispersion, solvent annealing, transparent electrode

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Introduction

High performance transparent electrodes are required for a wide range of optoelectronic devices, including lighting,¹ displays² and solar panels.³ For rigid applications, indium tin oxide (ITO) is the transparent conductor of choice, but its high cost, tendency to crack when flexed, and need for high temperature processing (>350 °C) are problematic for next generation applications employing flexible plastic substrates.⁴ Ambient-processable thin films of single-wall carbon nanotubes (SWNTs) have attracted considerable interest as a potential alternative to ITO due to their favorable balance of transparencies, conductivity, and work function and their resilience to repetitive flexing.⁵ SWNT transparent electrodes formed from (as-produced) 2:1 mixtures of semiconducting to metallic tubes have now reached⁶ performance levels approaching 60 Ω/sq. at 90% transmittance with conductivities of up to 12,000 S/cm. Initial conductivities are however much lower, typically ~1000 S/cm, and acceptable performance is only usually obtained after acid treatment to induce p-type doping of the semiconducting tubes⁷ and remove (insulating) dispersive agents.⁸ The use of acids in optoelectronic devices is liable, however, to leave residual contaminants that may damage adjacent semiconducting layers bringing into question the long-term stability of such devices.⁹,¹⁰

One of the most widely studied conducting polymer systems is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), obtained by chemically oxidizing the ethylenedioxythiophene (EDOT) monomer in the presence of (insulating) poly(styrene sulfonic acid). PEDOT itself is only sparingly soluble and the presence of water-soluble PSS during polymerization results in a stable PEDOT:PSS colloidal dispersion that is amenable to solution processing. The microstructure of highly conductive PEDOT:PSS is complex,¹¹ but is considered to consist of conductive PEDOT-rich grains loosely surrounded via a network of insulating PSS-rich chains.¹² To optimize the PEDOT:PSS conductivity, careful control of the PSS packaging is required to ensure that adequate electrical connectivity is maintained between individual PEDOT grains.¹³ The microstructure can be modified through a combination of solvent treatment and thermal annealing. For instance, the addition of polar solvents such as dimethyl sulfoxide (DMSO) to a solution of PEDOT:PSS at a weight ratio of 1:2.5
can increase\textsuperscript{14} the conductivity from around 0.1 to 1000 S/cm through beneficial solvent-induced changes in the morphology of the composite film during annealing, which lead to a more connected PEDOT network.\textsuperscript{15,16} It has previously been reported that vacuum-filtered SWNT/PEDOT:PSS films containing high weight loadings of SWNTs and the surfactant sodium dodecyl sulfate (SDS) exhibit enhanced electrical performance (80 $\Omega$/sq. at 75% transmittance) compared to stand-alone non-optimized PEDOT:PSS films (3.7 $\Omega$/sq. at 93% transmittance).\textsuperscript{17} An alternative route for developing SWNT/PEDOT:PSS electrodes is to directly disperse the SWNTs in the PEDOT:PSS, eliminating the need for insulating surfactants and vacuum filtration. In such an approach, the polymer chains are intended to act both as stabilizers for the initial SWNT dispersion and as conductive interconnects between the nanotubes in the deposited film. In this case, there is no need for either additional insulating surfactants or solubilization using aggressive acid treatments, which can introduce defects\textsuperscript{18} and so lead to reduced electrical performance of the SWNT network.\textsuperscript{19} A number of existing reports have commented on the possibility of directly dispersing SWNTs in PEDOT:PSS without quantifying this potential.\textsuperscript{20−22} In this paper, we demonstrate high final concentrations (>0.2 mg/ml) of SWNTs in PEDOT:PSS colloidal solutions (13 mg/ml polymer), confirming that PEDOT:PSS is indeed an effective dispersant for SWNTs.

**Results and discussion**

Mixed SWNT/PEDOT:PSS dispersions containing initial loadings (ILs) of 0 (reference), 1, 5 and 10 wt.% SWNTs, relative to the total solid content of PEDOT:PSS, were prepared by sonicating crude mixtures of the two materials for periods of 10, 20, and 40 min without additional surfactants, solvents, or other dispersing agents (see Methods). The solutions were centrifuged at 50,000 g in a variable axis rotor for three hours to induce sedimentation of high weight aggregates and impurities, and the top 90% of the supernatant was decanted and retained. High speed centrifugation was employed to maximize the fraction of individualized small diameter SWNTs present in the dispersion as this is a key requirement for the formation of highly conductive SWNT networks, although it inevitably reduces the quantity of SWNTs retained in the final dispersion.\textsuperscript{23} Aliquots were removed from each of the (strongly absorbing) samples and diluted by a factor of 30 to aid spectroscopic and visual analysis.

Fig. 1 shows absorption spectra for the various (diluted) solutions. There were no appreciable changes in the absorption spectra of the pure PEDOT:PSS reference samples after sonication and ultracentrifugation indicating that in all cases the PEDOT:PSS is largely unaffected by the SWNT dispersion procedure. The absorption characteristics of the 1 wt.% IL samples were indistinguishable from those of the pure PEDOT:PSS samples indicating the presence of only a small quantity of SWNTs in the final solution. The 5 and 10 wt.% IL samples, by contrast, showed clear differences with respect to pure PEDOT:PSS, with a general trend toward higher absorbance as the SWNT loading and sonication time were increased.

Subtracting the constant background due to PEDOT:PSS and assuming a (size-independent) mass attenuation coefficient of 30.3 $\pm$ 0.2 mg$^{-1}$ cm$^{-1}$ at 1035.3 nm for arc discharge SWNTs,\textsuperscript{24} it is possible to estimate the final loading (FL) of SWNTs present in the undiluted dispersions and hence to determine the processing yield, i.e. the retained fraction of SWNTs relative to the initial loading (see Fig. 2). For the range of SWNT loadings investigated here, 20 minutes of high power (150 W) sonication in PEDOT:PSS was required to achieve significant exfoliation of the nanotube aggregates/bundles. The FL increased steadily with increasing IL, reaching 0.23 $\pm$ 0.1 mg ml$^{-1}$ for an IL of 10 wt.% and a sonication time of 40 min. Lower IL tended to result in higher relative yields indicating more complete exfoliation of the SWNT bundles by the PEDOT:PSS.

The same general trends were qualitatively evident from visual inspection of the various solutions, with the samples showing a general increase in opacity with increasing sonication time and IL (see Fig. 3). Visual inspection of the final solutions indicated no agglomeration even for samples containing relatively high concentrations of SWNTs indicating good quality dispersions after the sonication/centrifugation procedure. It is therefore evident that PEDOT:PSS can effectively disperse SWNTs without the need for additional surfactants or solvents as a presumed result of coating by the high molecular weight, amphiphilic PSS chains. To our knowledge, this is the first report of the direct dispersion of SWNTs in PEDOT:PSS.
using high speed centrifugation, with previous studies having either involved the use of additional (insulating) surfactants to solubilize the nanotubes,\(^\text{17}\) or else having omitted the high speed centrifugation stage needed for the effective removal of larger agglomerates.\(^\text{25}\)

Thin PEDOT:PSS/SWNT films on glass were prepared by spin coating from the various undiluted solutions. Progressively thinner films of higher transparency were obtained by increasing the spin speed from 1000 to 7000 rpm. The thickness of the hybrid PEDOT:PSS/SWNT films ranged from 50 nm (transparency >85%) to 200 nm (transparency <75%) with no significant change in thickness recorded for different SWNT loadings, at a given transparency. To improve the conductivity of the PEDOT:PSS, we adopted a post-deposition strategy of drop-casting 1 ml of DMSO onto the pre-deposited films, and then removing it after a period of one minute by rotary drying (a similar method to that recently reported\(^\text{2}\)). This approach does not impair the wetting of the solutions to the underlying substrate, as is common when adding DMSO to a solution of PEDOT:PSS before deposition, and so ensures good film homogeneity. The films were also annealed at 150 °C for five minutes to remove residual DMSO and improve the PEDOT:PSS/SWNT microstructure. After treatment by DMSO, pure PEDOT:PSS films exhibited conductivities of up to 1500 S/cm, which represents a substantial improvement over both the initial conductivity of the untreated films (~1 S/cm) and the value listed under the manufacturer specification for conventional treatments, involving bulk incorporation of DMSO (~1000 S/cm). The SWNT-loaded PEDOT:PSS films were treated in a similar manner to obtain highly conductive films. We note that the conductivity of the PEDOT:PSS used in this work is substantially higher than that used in previous studies of SWNT/PEDOT:PSS composites.\(^\text{26−28}\)

Fig. 4 shows 5 μm × 5 μm tapping mode atomic force microscopy (AFM) images for thin films derived from 1 to 10 wt.% IL solutions subjected to either 10 or 40 min sonication. The increased SWNT density arising from higher initial SWNT loadings and longer sonication times is clear from the images and is in agreement with the solution-phase data in Fig. 1. However, the degree to which the SWNTs are connected to either the PEDOT or the PSS components is not clear.

The sheet resistance vs. transmittance trade-off characteristics are shown in Fig. 5 for films derived from 1, 5, and 10 wt.% IL solutions subjected to either 10 or 40 min sonication, spin coated in the range 1000–7000 rpm. Also shown for reference are the trade-off characteristics for the SWNT-free, solvent-enhanced PEDOT:PSS control films prepared from dispersions that had been subjected to 10 min sonication followed by ultracentrifugation at 50,000 g. The trade-off characteristics of the PEDOT:PSS films obtained were indistinguishable from those of films prepared from untreated PEDOT:PSS dispersions that had not been subjected to sonication or ultracentrifugation. For each IL value, a monotonic decrease in transmittance and sheet resistance was observed with decreasing spin speed, consistent with the increasing film thickness.
The films showed an increase in the sheet resistance to transmittance ratio with increasing SWNT loading and sonication time, with the lowest measured resistance at an acceptable level of transmittance for the PEDOT:PSS/SWNT films being 90 Ω/sq at 80% transmittance obtained from a 1 wt.% IL solution that had been subjected to 10 min sonication (FL = 0.033 mg/ml). This value compares to 70 Ω/sq for a PEDOT:PSS film containing no SWNTs, at the same transparency, suggesting the SWNTs do not enhance but rather reduce the performance of the films. To investigate the difference in conductivity between the PEDOT:PSS and SWNTs C-AFM was performed on the composite film to provide high-resolution spatial mapping of conductive and non-conductive regions of the film. As can be seen in Fig. 6 the SWNT network is visible in the contact mode image surrounded by PEDOT:PSS, as was the case for the tapping mode images in Fig. 6. The corresponding current scan shows the SWNT network as regions of lower conductivity inter-dispersed within the higher conductivity solvent-enhanced PEDOT:PSS. The current mapping confirms that the SWNTs are dispersed within the polymer matrix but that their presence does not confer any improvements in conductivity relative to the native, highly conductive PEDOT:PSS matrix.

The reduced performance of the PEDOT:PSS/SWNT films compared to the DMSO-treated PEDOT:PSS films is attributable to the inferior performance of undoped (non-acid treated) SWNTs which have higher sheet resistances (~200 Ω/sq. at 80% transmittance) than the DMSO-enhanced PEDOT:PSS used to disperse the SWNTs in this work (70 Ω/sq at 80% transmittance). While some previous reports have noted a reduction in sheet resistance after incorporation of SWNTs into PEDOT:PSS films, these reports did not use highly conductive PEDOT:PSS. A large increase in the conductivity of a low conductivity matrix is not necessarily a useful indicator.
Conclusion

In conclusion, PEDOT:PSS was found to be an effective dispersant for SWNTs, enabling uniform aqueous suspensions to be obtained at final concentrations of up to 0.23 mg/ml (>1% by weight relative to PEDOT:PSS) without recourse to additional surfactants. PEDOT:PSS was found to be resistant to high power sonication and ultracentrifugation with no change in mass or absorption spectrum observed making it an excellent candidate for the dispersion of SWNTs and other nano-materials. Thin films spin-coated from PEDOT:PSS/SWNT suspensions exhibited sheet resistances as low as 90 Ohm/sq at 80 % transmittance, slightly higher than DMSO-treated films of the pure PEDOT:PSS. This result compares favorably with previous composites combining vacuum filtered SWNTs with PEDOT:PSS (80 Ω/sq at 75% transmission17). However, an important limitation of the procedure used here is the presence of undoped, low conductivity, SWNTs since the PEDOT:PSS background and an extension coefficient. Aqueous solutions of PEDOT:PSS were purchased from Acheson for the PEDOT:PSS matrix does not allow the use of standard acid-based doping treatments. The type of acid-doping treatment used in many stand-alone SWNT films is not readily compatible with the PEDOT:PSS matrix. The implantation of new dopants, or the use of pre-sorted metallic tubes in PEDOT:PSS, might be expected to improve the performance of high conductivity solvent-enhanced PEDOT:PSS films.

Method

Arc-made SWNTs were purchased from Iijin Nanotech, Korea (now Hanwha Nanotech) with quoted purity, diameter, and length of 60–70 wt.%, 1.0–1.2 nm, and 20–30 nm, respectively. Aqueous solutions of PEDOT:PSS were purchased from H.C. Stark under the brand name Clevios PH 1000. The ratio of PEDOT to PSS was 1:2.5 and the total solid content was 1–1.3 wt.%. Mixtures of PEDOT:PSS and SWNTs were prepared by adding 1, 5 and 10 wt.% SWNTs (relative to the solid content of PEDOT:PSS) and subjecting them to 10, 20, and 40 min of tip sonication (Vibra-Cell VCX 750 at 20% power) in the Clevios suspension, cooled by iced water. Solutions were then centrifuged for three hours using a Beckman Coulter Optima L-100 XP Ultracentrifuge at 50,000 g (Rotor SW41).

A small volume of each solution was diluted by a factor of thirty prior to measuring the absorption spectra in a Perkin Elmer Lambda 25 spectrophotometer. The spectra were corrected for the PEDOT:PSS background and an extension coefficient of 30 ± 0.2 ml mg⁻¹ cm⁻³ at 1035 nm (Ref. 24) was assumed for the yield determination, correcting for the initial dilution. AFM images in Fig. 5 were obtained using a Veeco Dimension 3 series AFM in tapping mode. C-AFM images in Fig. 6 were obtained on ITO-coated glass slides using an Agilent 4300 AFM.

Glass substrates (15 mm × 15 mm) were cleaned with acetone and isopropl alcohol and were then subjected to 100 W oxygen-plasma treatment for 1 min to ensure cleanliness and good adhesion properties. The substrates were spin coated with the SWNT-PEDOT:PSS hybrid solutions at varying spin speeds (1000–7000 rpm) to control the thickness of the films. To enhance the conductivity of the PEDOT:PSS, DMSO was drop cast onto each film, left to stand for 1 min and spin dried for a period of approximately one minute. Finally, the films were annealed at 150 °C for five minutes to remove DMSO from the film and induce a conformational change in the PEDOT:PSS. The sheet resistances of the SWNT films were determined using a Keithley 4200 source meter connected to a four-point probe with an interprobe separation of 0.5 mm.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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