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Ashok K. Sundramoorthy\(^1\) (✉), Yi-Cheng Wang\(^1\), and Sundaram Gunasekaran\(^1\) (✉)

Nano Res., Just Accepted Manuscript • DOI 10.1007/s12274-015-0880-1
http://www.thenanoresearch.com on August 17, 2015

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Low-temperature solution process for preparing flexible transparent carbon nanotubes film and its application in flexible supercapacitors

Ashok K. Sundramoorthy*, Yi-Cheng Wang and Sundaram Gunasekaran*

Department of Biological Systems Engineering, University of Wisconsin-Madison, 460 Henry Mall, Madison, WI 53706, United States

A diazo dye (Congo red)-based simple solution process has been developed to prepare highly transparent flexible carbon nanotubes film with low sheet resistance (34±6.6 Ω/□) and high transmittance (81% at 550 nm), which is also shown suitable as a potential flexible supercapacitor electrode material.
Low-temperature solution process for preparing flexible transparent carbon nanotubes film and its application in flexible supercapacitors

Ashok K. Sundramoorthy¹(✉), Yi-Cheng Wang¹, and Sundaram Gunasekaran¹(✉)

¹ Department of Biological Systems Engineering, University of Wisconsin-Madison, 460 Henry Mall, Madison, WI 53706, UnitedStates

ABSTRACT

Single-walled carbon nanotubes (SWNT) are known for their high conductivity, mechanical strength, transparency, and flexibility, making them suitable for use in flexible electronics, transparent electrodes, and energy-storage and energy-harvesting applications. However, to exploit these properties, SWNT should be de-bundled in a surfactant solution for further processing and use. We report a new method to prepare SWNT-based transparent conducting film (TCF) using a diazo dye 3, 3'-[[1,1'-biphenyl]-4,4'-diyl] bis (4-amino naphthalene-1-sulfonic acid), commonly known as Congo red (CR), as a dispersant. About 20-nm-thick uniform TCFs were prepared on rigid glass and flexible polyethylene terephthalate (PET) substrates. The CR-SWNT dispersion and the CR-SWNT TCFs were characterized via UV-Vis-NIR, Raman spectroscopy, FT-IR spectroscopy, transmission electron microscopy (TEM), field-emission scanning electron microscopy (FE-SEM) and dynamic light scattering (DLS) measurements. The sheet resistivity of the CR-SWNT TCFs was about 34±6.6 Ω/□ at a transmittance of 81% (at 550 nm), which is comparable to that of indium tin oxide (ITO)-based films. Unlike SWNT dispersions prepared in common surfactants, such as sodium dodecyl sulfate (SDS), sodium cholate (SC), and Triton X-100, the CR-SWNT dispersion is amenable to forming TCF by drop coating. The CR-SWNT TCF is also very stable and maintains its very low sheet resistivity even after 1,000 consecutive bending cycles of 8 mm bending radius. Further, manganese dioxide (MnO₂) was electrochemically deposited on the CR-SWNT-PET film. The as-prepared MnO₂-CR-SWNT-PET film exhibited high specific capacitance and bendability, which make it a promising candidate as an electrode material for flexible supercapacitors.

1 Introduction

There is a growing demand for high quality transparent conducting films (TCFs) because of their use in flat-panel displays, electrochromic windows, photovoltaics, polymer solar cells,
hand-held devices, energy technologies, and biosensors[1]. Currently, indium tin oxide (ITO) film-coated transparent conducting materials are commonly used in applications where TCFs are needed. The ITO-based materials offer relatively low sheet resistance (~20 Ω/□) and fairly high transmittance (>80% at 550 nm)[2]. However, the cost of indium is on the rise due to increasing demand and limited availability[2]. Furthermore, ITO-based materials are unsuitable for high-flexibility applications, because they become brittle after a few bending cycles[3]. The market for transparent conductive film and glass is estimated to reach $6.3 billion in 2024[4, 5]. Therefore, other materials such as conducting polymers[6], metal wire/nanomesh[7, 8], nanofibers[9], single-walled carbon nanotubes (SWNT)[10-14], SWNT-metal hybrids[5, 15-17], and graphene[18] are being investigated as potential alternatives to ITO. Although conducting polymers such as polyaniline, polypyrrole and poly(3,4-ethylenedioxythiophene) exhibit conductivity similar to that of metal nanowires (copper and silver), their conductivity is sensitive to air due to redox doping process and will degrade significantly with time[19]. Further, conducting polymers absorb light in the visible range, giving a distinct color to the TCFs[19]. Metal nanowire/nanomesh-based TCFs offer high conductivity, but their transparency is usually a trade-off with sheet resistivity compared to ITO[20]. The high cost of metal (silver, copper etc.) is not conducive to large-scale cost-effective production of metal nanowire-based TCFs; moreover, their flexibility is also limited. Thus among various alternatives to ITO, SWNT-based TCFs are expected to gain significant market share because of their high mobility (100,000 cm²/Vs)[21], current carrying capacity (10⁶ A/cm²)[22], flexibility (without fracture)[23], and transparency in the visible range[5, 12].

SWNT-based TCFs can be prepared by various methods such as spin coating[24], dip coating[25], spray coating[26], bar coater[27] and by vacuum filtration[28]. However, since as-synthesized SWNT are highly hydrophobic bundles, they must be dispersed in a common surfactant such as sodium dodecyl sulfate (SDS), sodium cholate (SC), and Triton X-100 to take advantage of their numerous unique properties[29]. The sheet resistivity of TCFs prepared using SWNT dispersed in common surfactants is rather high. The electric conduction of SWNT film (at SWNT-SWNT junctions) is dominated by tunneling[30]. The thin insulting surfactant (or polymer) layer surrounding the nanotubes prevents direct contact between the SWNT[31]. Since the adhering surfactants could not easily be rinsed away[32], the SWNT films were annealed at a high temperature or acid-washed to remove the adhering surfactant and reduce the sheet resistance[33-35]. Both annealing and acid washing will damage the structure of SWNT, which also affects the conductivity of nanotubes[36]. Furthermore, the requirement of high-temperature annealing treatment precludes using flexible substrates such as polyethylene terephthalate (PET) and polydimethylsiloxane (PDMS). Therefore, the SWNT-based films were first prepared on a solid substrate and annealed before being transferred onto a flexible substrate[11, 37, 38].

By considering the potentials of SWNT and the need for ITO-free TCFs, it is necessary to develop an effective solution-based process that can be used for large-scale production of flexible SWNT film with low sheet resistivity and high transparency. Herein, we present such a method using 3,3’-(1,1-biphenyl)-4,4’-diyl)bis(4-aminonaphthalene-1-sulfonic acid), commonly known as Congo red (CR), to disperse SWNT. CR is a symmetrical linear molecule (Fig. 1(a)) soluble in both aqueous and organic solvents, such as dimethylformamide (DMF) and ethanol. Due to the strong hydrophobic
polycyclic aromatic functional groups with ionizable sulfonic groups, CR was expected to disperse SWNT in aqueous solution[39]. We extensively studied the ability of CR as a dispersant for SWNT by comparing it with that of SDS, SC, and Triton X-100.

We used SWNT dispersed in CR (CR-SWNT) to form a thin-transparent film with very low sheet resistivity (34±6.6 Ω/□) and high transparency (transmittance ~81%). CR-SWNT could be used to prepare TCFs by drop coating or spin coating on rigid and flexible substrates. It is worth mentioning that drop coating is not suitable for SWNT dispersed in SDS (SDS-SWNT), SC (SC-SWNT), and Triton X-100 (Triton-SWNT). Our CR-SWNT-based TCFs are viable alternatives to ITO-based materials or carbon-based flexible conducting films, especially for applications requiring flexible substrates. To our knowledge, this is the first extensive study on using CR as a dispersant for preparing SWNT-based TCFs.

Flexible energy storage devices are important for a wide range of applications such as flexible electronic displays, wearable devices, and flexible solid-state supercapacitors[40-43]. Specifically, transparent electrodes play a major role in preparing entirely transparent flexible organic light-emitting diodes, field-effect transistors, energy-harvesting and flexible power sources[44-46]. Supercapacitors with flexible power source are required to realize flexible energy-storage devices that can function under considerable physical deformation and stress[41, 47]. Ge et al. reported preparing transparent and flexible electrodes and supercapacitors using polyaniline/SWNT composite thin films with specific capacitance of 55 F·g⁻¹ at a current density of 2.6 A·g⁻¹ [48]. Due to the exceptional pseudo-capacitance properties of manganese dioxide (MnO₂), it is popularly used in the preparation of supercapacitors. Recently, ultralight and flexible MnO₂/carbon foam composites[49], manganese ferrite (MnFeO₄)/graphene-based flexible supercapacitors[50], MnO₂/stainless steel-based mesh-supercapacitor[51], electrochemically grown large-area alpha-MnO₂ nanoflower arrays on flexible graphite paper[52] and solvothermal method to fabricate MnFeO₄/graphene hybrids on flexible graphite sheets have been demonstrated[50].

In this work, we electrochemically deposited MnO₂ onto our CR-SWNT-PET flexible electrode to demonstrate the potential use of our TCFs in flexible energy-storage applications such as supercapacitors. We also investigated specific capacitance, galvanostatic charging-discharging, bendability, and stability of the as-prepared MnO₂-CR-SWNT-PET electrode.

2 Experimental

2.1 Materials

Pristine P2-SWNT (arc-discharge) was purchased from Carbon Solutions, Inc (Riverside, CA, USA). CR was purchased from MP Biomedicals, LLC. (Solon, OH, USA). Sodium cholate hydrate (SC) and Triton™ X-100 were received from Alfa Aesar (Ward Hill, MA, USA). Manganese (II) acetate, ethanol and dimethylformamide (DMF) were from Sigma-Aldrich (St. Louis, MO USA). Sodium dodecyl sulfate (SDS) was received from AMRESCO® LLC (Solon, OH, USA). Sodium sulfate (Na₂SO₄) was from FisherChemicals (Fair Lawn, NJ, USA). All other reagents were of analytical grade and used without further purification. In all experiments, deionized water with resistivity of 18 MΩ·cm was used.

2.2 Preparation of CR-SWNT dispersion

P2-SWNT (5 mg) were mixed in 10 mL of 1 mM CR
solution and bath-sonicated for 10 min. The mixture of CR and SWNT was further ultrasonicated in a 130-W Ultrasonic processor for one hour using ice bath to control temperature of the mixture. Finally, the CR-SWNT was centrifuged at 12,000 rpm for one hour and the supernatant was collected and used. For comparison, supernatants of pristine P2-SWNT dispersed in 1% SDS, 1% SC, and 1% Triton X-100 were similarly collected.

### 2.3 Preparation of CR-SWNT-based TCFs

SWNT films were prepared on rigid glass, flexible PET, or PDMS substrates by spin coating or drop coating of CR-SWNT dispersion. For spin coating, CR-SWNT was dropped onto the flat substrate, which was spun at 2000 rpm. The CR-SWNT-coated substrate was dried at 60 °C for 30 min to 1 h and washed with DMF and ethanol multiple times, and then using deionized water (it is not recommended to directly wash with water before DMF/ethanol washing). Finally, the CR-SWNT-coated substrates were again dried at 60 °C for 30 min. For drop coating, CR-SWNT, SDS-SWNT, or Triton-SWNT were pipetted and allowed to uniformly spread on the substrate for 2 min before drying at 60 °C in an air oven.

### 2.4 Characterization of CR-SWNT

The films were characterized using FE-SEM (Leo 1530 Field Emission SEM), LabRAM Aramis (Horiba JobinYvon) confocal Raman microscope, and Bruker’s AFM microscope. DLS analysis was performed using 90 Plus Particle size analyzer (Brookhaven Instruments). A UV-Vis-NIR spectrophotometer (Lambda 25, PerkinElmer) and a Fourier transform-infrared (FT-IR) spectrometer with universal attenuated total reflectance (ATR) sampling accessory (Spectrum 100, PerkinElmer) were used for characterizing CR-SWNT and TCFs. Transmittance of the films was measured after baseline subtraction with bare glass or PET substrate. Thus, %transmittance reported is solely due to the SWNT films. A spin coater (6800 Spin Coater Series, Specialty Coating Systems, Indianapolis, Indiana, USA) was used to spin coat nanotubes. CR-SWNT was centrifuged using Eppendorf centrifuge 5415C. Contact angles were measured using Dataphysics OCA 15 unit. The Hewlett Packard 4142B Modular DC source/monitor connected HP 34401A multimeter with a contact four-point probe station (Cascade Microtech Inc., Beaverton, Oregon, USA) was used to measure the sheet resistivity of the film. Electrochemical measurements were performed using an electrochemical analyzer (CHI 660C, CH Instrument Inc., Austin, TX, USA).

### 2.5. Preparation of MnO₂-CR-SWNT-PET electrode

To prepare a flexible, indium-free supercapacitor, MnO₂ was potentiodynamically deposited onto the CR-SWNT-PET substrate through cyclic voltammetry (CV) at 50 mV.s⁻¹ by potential sweeping between 0.0 and 1.4 V for 10 cycles. Electrochemical deposition of MnO₂ was achieved using CR-SWNT-PET as a working electrode in a three-electrode cell setup with 50 mM manganese(II) acetate and 100 mM Na₂SO₄ solution. Platinum wire and silver/silver chloride (Ag/AgCl) (in 3 M KCl) were used as counter and reference electrodes, respectively. An alligator clip was connected with a copper foil to the CR-SWNT-PET film to ensure good electrical contact. After successful electrochemical deposition, MnO₂-CR-SWNT-PET was thoroughly washed with deionized water and dried in an air oven at 60 °C for 30 min. Surface morphology of the MnO₂ film was characterized via FE-SEM. To study the electrochemical properties of the MnO₂-CR-SWNT-PET, Nafion® (5% w/w) solution (Fuel Cell Earth Llc., Woburn, MA, USA) was placed on the top of the film[53]. After solvent evaporation, Nafion layer was covered the film and
served as the separator. In addition, MnOۡ/CR-SWNT-PET was soaked in distilled water for 30 min, and then electrochemical studies were performed in 100 mM NaۡSOۡ۳ solution. We used a three-electrode system used for CV measurements described above. The unstable first cycle of CV measurements was discarded.

Electrochemical stability of electrode materials is important for flexible supercapacitor applications. Our CR-SWNT-PET film had superior flexible properties. To verify if the MnOۡ/CR-SWNT-PET film was stable when flexed, test was performed by bending it back-and-forth manually for 100 times, with a bending radius of 8 mm.

3 Results and discussion

3.1 Preparation of CR-SWNT-TCF

Our scheme for preparing CR-SWNT-based TCFs on a rigid (glass) and flexible (PET or PDMS) substrates by drop coating or spin coating is depicted in Figure 1(b). As shown in Figure 1(c), TCFs prepared using CR-SWNT formed a uniform thin film after oven drying for 30 min at 60 °C. After DMF/ethanol washing, CR-SWNT film was very stable and strongly adhered to the substrate even after repeated washings with water. However, films could not be prepared similarly using SDS-SWNT and Triton-SWNT, as they became aggregated and partly sloughed off from the substrate after washing with DMF, ethanol, and water (Figs. S1(a), and (b)). Our observation was similar to those of others who reported pre-functionalization or treatment of the substrate (with 3-aminopropyltrimethoxysilane) was required to form stable SWNT films using common surfactant dispersions[17].

Since CR is soluble in DMF, we also attempted to disperse SWNT in both DMF and DMF with 1 mM CR (CR-DMF) solutions. Stable dispersions of SWNT were obtained both in DMF and CR-DMF; however, the dispersibility of SWNT was higher in CR-DMF than in DMF. Furthermore, films were easily formed on PDMS substrate by drop coating of SWNT-CR-DMF dispersion (Fig. S2(a)), which was not the case with the SWNT-DMF dispersion (Fig. S2(b)). This indicates that the addition of CR affords the formation SWNT film and its adherence on the PDMS substrate.

3.2 Adhesion properties of CR-SWNT dispersion

The consistencies of the CR solution and all SWNT dispersions were similar. However, the CR aqueous solution and the CR-SWNT tended to adhere to the walls of 1.5-mL microcentrifuge tube, which was evidenced by inverting the tubes (Fig. 2(a), a, a’ and b, b’). While SDS-SWNT and Triton-SWNT descended (Fig. 2(a), c, c’ and d, d’), the CR solution and CR-SWNT did not (Fig. 2(a)). This suggests that CR has an inherent ability to form a matrix structure with certain short-range binding affinity to the hydrophobic surface. Presumably, the hydrophobic backbone of CR molecules interacts with hydrophobic surface and position self-assembly of SWNT on the substrate. This could be the reason why we are able to form TCFs on substrates with CR-SWNT, unlike with SDS-SWNT or Triton-SWNT (Fig. 2(a) and Fig. S2).

3.3 UV-Vis-NIR, Raman and FT-IR characterization

The UV-Vis-NIR spectra of the CR-SWNT exhibited a red-shift in the absorption peak of CR, from 497 nm to 502 nm (Fig. 2(b)), suggesting a strong charge transfer between CR and SWNT in aqueous solution. UV-Vis-NIR spectra of SC-SWNT show two distinct semiconducting bands (S22, S33) and one metallic band (M11), which are characteristics of SWNT prepared by arc-discharge (Fig. 2(b), curve c)[54]. However, S22 and M11 bands are suppressed for CR-SWNT due to strong adsorption of CR on the nanotubes (Fig. 2(b), curve b).
To verify the nature of interaction between SWNT and CR, Raman spectra of CR-SWNT film, CR powder (control) and pristine SWNT were obtained (Fig. 3(a)). Comparing the spectra of CR-SWNT film and pristine SWNT (Fig. 3(a)), we notice that the G band had up-shifted from 1591 to 1596 cm\(^{-1}\) and that the intensity of G band decreased substantially, due to the strong electron charge transfer from CR to SWNT (Fig. 3(a) and Fig. S3(a))\(^{[55-57]}\). Raman peaks of CR were also present in the spectra of CR-SWNT film even after repeated washing with DMF and ethanol, which further confirmed strong non-covalent binding between CR and the nanotubes (Fig. 3(a) curve ii). However, Raman peaks of CR disappeared when the CR-SWNT film on glass substrate was thermally annealed at 500 °C in a vacuum furnace for 10 min, but the disorder (D) band (at 1312 cm\(^{-1}\)) slightly increased (Fig. S3(b), curve ii). This is attributed to covalent reaction happening on the nanotubes by radicals generated from CR at high temperature. Thermal annealing step decreased the inter-tube contact resistance, consequently the SWNT films prepared on a glass substrate showed sheet resistivity of 366±138Ω/\(\square\) at a transmittance of 87 % (at 550 nm) (Fig. 3(b)).

The interaction between CR and SWNT was also confirmed by FT-IR. The spectrum for pristine SWNT (Fig. 4) were similar to those previously reported\(^{[58]}\), without any distinct features in the range of 600 to 4000 cm\(^{-1}\) possibly due to the high quality of the P2-SWNT. The FT-IR spectrum for CR showed a broad and strong absorption band at 3464 cm\(^{-1}\) (N–H bonds), with several other peaks at 1041, 1176 (the stretching vibration of S=O due to \(-SO_3^-\)), 1597 (assigned to stretching vibration of \(-N=N-\) bond), 1352 and 1222 cm\(^{-1}\) (the stretching vibrations of \(=C-N=\) group adjacent to aromatic ring). Other bands located at 904, 832, 749 and 697 cm\(^{-1}\) were assigned to aromatic rings (C–H) of CR (Fig. 4(a), (b)). Significant new bands were observed in the spectrum for CR-SWNT film (Fig. 4(a) and (b)), confirming that some functional groups are attached to the nanotubes. The S=O stretching vibration observed in the CR spectrum was present in the CR-SWNT spectrum, but red-shifted to a lower wavenumber of 1030 cm\(^{-1}\), perhaps due to the \(\pi-\pi\) stacking between SWNT and CR molecules.

### 3.4 SEM, AFM, TEM and DLS measurements

We further characterized the CR-SWNT-TCF using FE-SEM and AFM. The FE-SEM micrographs (Figs. 5(a), (b)) show a dense network of SWNT forming a 20-nm-thick film on the substrate. The CR-SWNT film and SC-SWNT film on copper grid were also determined by measuring the diameters of SWNT and uniformity of films using transmission electron microscopy (TEM) (Fig. 5(c), (d)). The average diameters of individual SWNT and nanotube bundles in the CR-SWNT film were in the range of 1.2 to 7 nm (Fig. 5(c)), which was smaller than those in the SDS-SWNT film (~1.2 to 30 nm; individual tubes to bundles) (Fig. 5(d)). The diameter of arc-discharge SWNT was in the range of 1.2 to 1.6 nm\(^{[59]}\). Thus, the presence of up to 7 nm diameter entities in our film clearly indicates that bundles of up to three to four nanotubes exist. However, a highly dense film network was observed for CR-SWNT film compared to SC-SWNT film.

To ascertain why CR-SWNT could form uniform nanotube network film on rigid and flexible substrates without any surface treatment, we investigated further. The CR solution and SDS-SWNT and SC-SWNT formed concave meniscus in a plastic cuvette (Fig. S4). Adhesion is responsible for meniscus formation, and this has to do in part with fairly high surface tension of water. When CR, SDS and SC were dispersed in water, the surface tension decreased; further, due to poor interaction between the dispersions and the cuvette, a concave meniscus was formed (Fig. S4). However, with CR-SWNT the concavity of the meniscus was not obvious, which we believe was due to the
attraction of CR molecules to the hydrophobic molecules on the cuvette surface (Fig. S4 (b)). Sa et al. reported that SDS-SWNT would form micelles in the solution[60]. When SWNT dispersed in surfactant solution, the individual or bundles of SWNT were wrapped and separated completely by the surfactant molecules[60]. Charged SWNT were stabilized in water due to the repulsive forces of negatively charged polar head groups of SDS. Due to hydrophobicity, SWNT were lifted above the air-water interface[61]. In our case, with the addition of SWNT in CR solution, hydrophobic part of CR (both biphenyl and naphthalene rings) would interact with SWNT (via hydrophobic interaction)[62]. As shown in Fig. S4(b), almost a flat meniscus was observed due to the strong molecular repulsion between SWNT. We assume that ionized polar head group of CR (SO\textsuperscript{−}) stays dipped in water, while the hydrophobic CR-SWNT part tends to escape projecting toward the air-water interface. That is why an almost flat air-water interface was observed with the CR-SWNT (Fig. S4(b)).

Apparently, as shown in Figure S5, at lower concentrations (2.9 and 28.6 µM) the CR molecules do not interact and adhere sufficiently to the walls of the microcentrifuge tube that was observed at higher concentrations (≥57.1 µM). This clearly shows strong adhesion between CR molecules and hydrophobic surfaces[63]. In addition, a drop of CR and SC solutions and CR-SWNT, SDS-SWNT, and SC-SWNT were placed on PET substrate to demonstrate strong adhesion of CR on PET. Both CR solution and CR-SWNT formed an almost uniform film upon drying (Table S1, (a), (b)). In contrast, SC, SC-SWNT, and SDS-SWNT became aggregated (Table S1 (c), (d), (e)). We noticed that after removing free CR molecules by washing with DMF and water, a very thin layer of CR remained, which showed that CR binds with PET. This was confirmed by obtaining UV-Vis spectra of bare PET, PET after applying a thin film of CR (CR-PET), and CR-PET after washing with DMF. For CR-PET, before DMF washing, a strong broad absorption peak was observed from 400 to 600 nm (centered at 500 nm) (Fig. S6), and after DMF washing, about 2% decrease in transmittance was observed, which indicates that a thin-layer of CR is still attached to PET (Fig. S6). The amine and sulfonic acid groups of CR apparently interacted with the substrate and formed a uniform CR-SWNT film after drying (without any additional surface treatment).

The distribution of hydrodynamic radius of single or bundles of nanotubes present in CR-SWNT, SC-SWNT, and SDS-SWNT were measured by DLS, which showed that the mean diameter of nanotube bundle was larger in CR-SWNT (104 nm) than in SC-SWNT and SDS-SWNT (70 and 75 nm, respectively) (Fig. 6). These values represent the hydrodynamic diameter of SWNT bundles plus any adhering surfactant molecules. The presence of nanotube bundles in CR-SWNT indicate that they might be wrapped with the supramolecular structure of CR molecules.

3.5 Sheet resistance, flexibility and contact-angle measurements

The SWNT films prepared on a PET substrate (30 mm × 30 mm) by spin coating of CR-SWNT is shown in Figure 7(a). This as-prepared CR-SWNT-PET film is conductive with a sheet resistivity of 183.6±19.7 Ω/□ at 71% transmittance (at 550 nm) (Fig. S7 and Fig. 7(b), red curve). The effect of SWNT density on the conductivity of the film was studied by AFM (Fig. 7(c)). SWNT films with lower density of nanotubes were also prepared by adjusting the volume of CR-SWNT for comparison (Fig. S8). The sheet resistivity of the lower-density (16 nanotubes/µm\textsuperscript{2}) film (1.56 kΩ/□ at 90% transmittance) was much higher than that of the higher-density (>50 nanotubes/µm\textsuperscript{2}) film (183.6 Ω/□ at 71% transmittance).
The hydrophobicity of the CR-SWNT-PET film was studied after drying under flow of nitrogen gas. The highest contact angle value of the as-prepared film was ~100° (Fig. 59). The hydrophobicity of the film may arise due to the synergistic effect of long aromatic backbone of CR and SWNT, which may be preferable for flexible electronic display applications[28].

The sheet resistivity of the CR-SWNT-PET film may be further lowered by treating with nitric acid (HNO₃)[64]. We immersed the film in HNO₃ for 30 min at room temperature. The UV-Vis-NIR transmittance spectra showed that after the HNO₃ treatment and following washing with water, the CR molecules were removed (Fig. 7(b), blue curve). The absorption intensity of the inter-band energetic transition of S22, S33 and M11 of SWNT were almost bleached off, which shows the acid-doping effect of nanotubes[65]. The sheet resistivity of the film after HNO₃ treatment was 34±6.6 Ω/□ (at a transmittance of 81% at 550 nm) (Fig. 7(d)), which is several folds better than that of the untreated film (183.6 ±19.7 Ω/□) (Fig. S7). Furthermore, the sheet resistivity of the film remained virtually unchanged even after 1,000 bending cycles at bending radius of 8 mm, confirming the high flexibility and stability of CR-SWNT-PET TCFs (Fig. 7(d)).

To demonstrate the potential application of CR in preparing TCFs, we attempted to prepare TCF films by drop coating of 500 µL CR-SWNT, Triton-SWNT, and SDS-SWNT on PET substrates (as shown in Fig. 1(b) and experimental section 2.3). While a uniform TCF film was obtained with CR-SWNT, both Triton-SWNT and SDS-SWNT became aggregated during drying at 60 °C for 30 min. Sheet resistance and transparency of these films showed that the lowest sheet resistance of 57.69±23.50 Ω/□ at transparency of 73.95±6.12 % was obtained for CR-SWNT-PET (Table S1 and Fig. S10). These results confirm that CR is the best dispersant, among those we studied to prepare SWNT-based TCFs. In addition, estimated costs of preparing TCFs reveal the cost-effectiveness of our CR-SWNT-PET (Table S2). Hence our TCF is suitable for economical large-scale production of TCF for industrial applications, without requiring processes such as vacuum deposition, thermal annealing etc.

3.6 CR-SWNT TCF in Flexible Supercapacitors

The CR-SWNT TCF (width 1 cm × length 3 cm) acquired yellow color after electrodeposition of MnO₂ (Fig. 8). As shown in Figure 9(a), during first anodic scan, two anodic peaks were observed at 0.81 and 1.1 V, which correspond to the two distinct electrochemical oxidation mechanisms of manganese and deposition of MnO₂ on CR-SWNT-PET film (Equations 1-3)[66, 67]. With the increasing cycle number, both anodic (at 1.1 V) and cathodic (at 0.3 V) peaks increased, which indicated successful deposition of MnO₂ on the CR-SWNT-PET film according to the following equations (Equations 1-3) (Fig. 9(a)).

\[
\text{Mn}^{2+} \rightarrow \text{Mn}^{3+} + \text{e}^- \quad (1)
\]

\[
\text{Mn}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{MnOOH} + 3\text{H}^+ \quad (2)
\]

\[
\text{MnOOH} \rightarrow \text{MnO}_2 + \text{H}^+ + \text{e}^- \quad (3)
\]

FE-SEM image of MnO₂-SWNT-PET showed homogeneous and compact layer of MnO₂ particles (Fig. 8(c)), which imply high electrical conductivity of our CR-SWNT-PET film. The CVs of the CR-SWNT-PET film before and after MnO₂ deposition in 100 mM Na₂SO₄ solution at 10 mV/s are compared in Figure 9(b). From the CV data, the specific capacitance (Cs, F.g⁻¹) of the MnO₂-CR-SWNT-PET film at different scan rates was calculated using equation 4 [68]:

\[
Cs = \frac{1}{mn(V_a - V_c)0.8} \int_{0.3}^{0.8} I(V) d(V)
\]
Where, \( m \) is the mass of MnO\(_2\) (1.5 mg), \( v \) is the scan rate, \( (V_a-V_c) \) is the potential window of CV, and \( I(V)d(V) \) is half of the integrated area under the CV curve.

Electrochemical impedance spectroscopy (EIS) was further used to study changes in conductivity of CR-SWNT-PET electrodes after MnO\(_2\) deposition. EIS was performed in 0.1 M KCl solution containing 5 mM [Fe(CN)\(_{6}\)]\(^{3-/4-}\) at 0.2 V vs. Ag/AgCl for the CR-SWNT-PET and MnO\(_2\)-CR-SWNT-PET electrodes. The Nyquist plots of the impedance spectra obtained are presented in Fig. 8(d). An intercept at the \( Z' \) (real axis) in high-frequency region corresponds to the ohmic electrolyte resistance (\( R_s = \sim 65 \, \Omega \)). In addition, EIS spectra of both electrodes contain a semicircle in the high frequency region (due to the charge-transfer process, \( R_s \)) and a straight sloping line in the low frequency region (due to the diffusion of potassium ions (\( R_a \)) into active material). As expected, the calculated \( R_a \) value of CR-SWNT-PET electrode increased from 427 \( \Omega \) to 611 \( \Omega \) after MnO\(_2\) coating.

Further, after MnO\(_2\) coating on CR-SWNT-PET electrode, a uniform layer of polymer electrolyte was formed by drop coating of Nafion solution (see details in experimental section 2.5). Finally, Nafion/MnO\(_2\)-CR-SWNT-PET electrode was used to test its electrochemical properties. A substantial increase in the Cs value was obtained after MnO\(_2\) deposition (34.53 F.g\(^{-1}\) compared to 1.6 F.g\(^{-1}\)) (Fig. 9(b)).

### 3.7 Effect of CR-SWNT film thickness on MnO\(_2\) deposition

To ascertain the effect of CR-SWNT film thickness on MnO\(_2\) deposition, we prepared three CR-SWNT-PET electrodes with thicknesses of 30, 60 and 140 nm. The film thickness was measured using AFM (Fig. S11, (a), (b), (c)). Then, CR-SWNT-PET (width 1 cm \( \times \) length 1 cm) was exposed to electrolyte solution containing 50 mM manganese acetate and 100 mM Na\(_2\)SO\(_4\) at 50 mV/s scan rate for 10 cycles (Fig. 9(a)). After successful electrodeposition of MnO\(_2\) on each CR-SWNT-PET electrode, CVs were recorded individually in 100 mM Na\(_2\)SO\(_4\) solution at a scan rate of 10 mV/s and compared (Fig. S11 (d), curves (a), (b), (c)). The Cs values of 30-, 60-, and 140-nm thick MnO\(_2\)/CR-SWNT-PET were calculated as 3.76, 10.98, and 7.13 F.g\(^{-1}\), respectively. Thus, Cs appears to reach a peak in between 60 and 140 nm substrate film thickness. The decrease in Cs value after reaching a peak may be due to the complete coverage and saturation of MnO\(_2\) layer on the CR-SWNT film. We used 60-nm-thick CR-SWNT-PET film for further electrochemical studies.

### 3.8 Effect of scan rate and galvanostatic charge/discharge studies

The effect of scan rate (from 10 to 250 mV/s) on the CVs of Nafion/MnO\(_2\)-SWNT-PET electrode showed rectangular (at lower scan rates) and quasi-rectangular (at higher scan rates) shapes without any peaks, which indicated an ideal electrical double layer capacitance and fast charging/discharging of the Nafion/MnO\(_2\)-CR-SWNT-PET electrode (Fig. 9(c)). As shown in Figure 9(d), the highest Cs was recorded (34.53 F.g\(^{-1}\)) at a low scan rate of 10 mV/s, with Cs declining with increasing scan rate due to direct impact on the diffusion time of cations into the matrix, which leads to a sharp decrease in the available capacity (Fig. 9(d))[70].

Furthermore, the CVs recorded before and after consecutive 100 bending cycles (Fig. S12) of MnO\(_2\)-CR-SWNT-PET electrode in 100 mM Na\(_2\)SO\(_4\) solution showed no significant changes in the capacitance (Fig. 10(a)). Figure 10(b) shows the galvanostatic charge/discharge curve of
Nafion/MnO$_2$-CR-SWNT-PET in 100 mM Na$_2$SO$_4$ between 0 and 0.8 V at various current densities. The charging curves were almost symmetric to their corresponding discharging curves at current densities from 140 to 700 mA$\cdot$g$^{-1}$, which is indicative of good capacitive behavior of the flexible Nafion/MnO$_2$-CR-SWNT-PET electrode. In addition, the symmetrical linear triangle shaped charging/discharging curves indicate good reversibility and increased Faraday redox reaction of the electrodeposited MnO$_2$ (Fig. 10(c)). The electrochemical stability of Nafion/MnO$_2$-CR-SWNT-PET electrode was investigated by potential cycling in the range of 0 to 0.8 V in 100 mM Na$_2$SO$_4$ aqueous solution (Fig. 10(d)). We found that the Nafion/MnO$_2$-CR-SWNT-PET retained about 80% of the initial capacitance after 600 cycles. Thus, our CR-SWNT-PET is highly conductive and flexible, and suitable for manufacturing flexible supercapacitors.

4. Conclusions

We described a fairly simple and inexpensive method to prepare SWNT-based TCF using CR as a dispersant. Our method allows casting films on rigid and flexible substrates without surface treatment by either drop coating or spin coating. The sheet resistivity and transparency of our SWNT film ($34\pm 6.6$ $\Omega/\square$ at a transmittance of 81% (at 550 nm)) are much better than those reported in the literature (see Table S3), and indeed comparable to those of ITO-based films. The CR-SWNT-PET is useful as a highly conducting electrode in electrochemical system, and can be used as a potential alternative to ITO-free electrode. The potential use of our TCF for energy-storage application was demonstrated by preparing and testing a highly flexible supercapacitor electrode by electrodepositing MnO$_2$ on the CR-SWNT-PET substrate.

Acknowledgments

The authors acknowledge the support of the Wisconsin Alumni Research Foundation.

Electronic Supplementary Material:

Supplementary material (SWNT-TCF images of SDS, SC, Triton-X-100 and DMF, Raman spectra, photograph showing meniscus, different concentrations of CR in water, sheet resistivity of CR-SWNT-PET, AFM results, contact angle measurements, CR-SWNT, SDS-SWNT and Triton-SWNT TCFs, CR-SWNT film thickness measurements, flexibility testing, cost estimation table and sheet resistivity comparison) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-****-**** (automatically inserted by the publisher).

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Figure 1 (a) Chemical structure of CR, (b) scheme for preparing SWNT-based TCFs using CR-SWNT dispersion on rigid glass and flexible PET substrates, and (c) CR-SWNT TCF preparation by drop coating.
Figure 2. (a) CR solution (a, a’), and dispersions of CR-SWNT (b, b’), SDS-SWNT (c, c’), and Triton-SWNT (d, d’). (b) UV-Vis-NIR spectra of (a) CR solution and dispersions of (b) CR-SWNT and (c) SC-SWNT.
Figure 3 (a) Raman spectra of (i) CR powder (control), (ii) CR-SWNT and (iii) pristine-SWNT samples (using 633 nm excitation laser). (b) Transmittance (measured after baseline subtraction with bare glass) of CR-SWNT-film-coated glass substrate.
Figure 4 (a) FT-IR spectra of CR powder (control), pristine P2-SWNT and CR-SWNT film. (b) Enlarged view of the curves in (a) from 600 to 2000 cm\(^{-1}\).
Figure 5 FE-SEM (a, b) images of as-prepared CR-SWNT films on glass substrate and TEM images of (c) CR-SWNT and (d) SC-SWNT films on TEM copper grid.
Figure 6 Hydrodynamic radius (size) measurement of CR-SWNT, SC-SWNT, and SDS-SWNT dispersions.
Figure 7: (a) CR-SWNT-film-coated PET substrate. (b) Transmittance measured after baseline subtraction with bare PET of CR-SWNT-PET before and after washing in nitric acid solution. (c) AFM image of CR-SWNT-PET (with height measurement curve superimposed). (d) Sheet resistivity of acid-treated CR-SWNT-PET as a function of number of bending cycles (bending radius = 8 mm).
Figure 8  CR-SWNT-PET electrode (a) before and (b) after MnO$_2$ deposition and (c) SEM image of deposited MnO$_2$ (b). (d) Electrochemical impedance spectroscopy of CR-SWNT-PET and MnO$_2$-CR-SWNT-PET in 0.1 M KCl solution containing 5 mM [Fe(CN)$_6$]$^{3-/4-}$. Applied potential was 0.2 V vs. Ag/AgCl with frequency range from 0.01 to 100,000 Hz and amplitude of 5 mV.
Figure 9 (a) Electrochemical deposition of MnO$_2$ onto a CR-SWNT-PET film from a solution containing 50 mM manganese acetate and 100 mM Na$_2$SO$_4$ at 50 mV/s scan rate. (b) Comparative cyclic voltammograms for Nafion/MnO$_2$-CR-SWNT-PET and CR-SWNT-PET in 100 mM Na$_2$SO$_4$ solution at 10 mV/s. (c) Effect of scan rate for Nafion/MnO$_2$-CR-SWNT-PET film in 100 mM Na$_2$SO$_4$ solution at (from inner to outer) 10, 20, 50, 100, 150, 200, and 250 mV/s. (d) Variation of specific capacitance with scan rate for Nafion/MnO$_2$-CR-SWNT-PET electrode.
Figure 10 (a) Comparison of cyclic voltammograms of MnO$_2$-CR-SWNT-PET electrode before (blue curve) and after (red curve) 100 bending cycles (bending radius= 8 mm), Scan rate = 10 mV/s using 100 mM Na$_2$SO$_4$ as electrolyte. (b) Galvanostatic charge/discharge curves of Nafion/MnO$_2$-CR-SWNT-PET electrode at (a) 700, (b) 350, (c) 210, and (d) 140 mA·g$^{-1}$. (c) Galvanostatic charge–discharge curves (10 cycles) for Nafion/MnO$_2$-CR-SWNT-PET electrode at a current density of 140 mA·g$^{-1}$. (d) Cycle life of Nafion/MnO$_2$-CR-SWNT-PET electrode in 100 mM Na$_2$SO$_4$ solution.