Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information for "Electrical and Optical Properties of 4-*N*,*N*-dimethylamino-4′-*N*′-methyl-stilbazolium tosylate (DAST) Modified by Carbon Nanotubes"

1. DAST synthesis:

In this work, DAST was synthesized through the following procedures: (1) 10.3 mL (0.105 mol %) picoline and 15.9 mL (0.105 mol %) methyl toluene sulfonate were added to 200 mL toluene, and the mixture was stirred in a 500 mL round-bottom flask of a home-built Dean-Stark apparatus; (2) The mixture of (1) was heated until it crystallized as a while salt that is insoluble in toluene; (3) During boiling, dimethyl-formamide (DMF) solvent was added until the mixture of (2) became a clear solution; (4) After getting the clear solution, 10.3 g (0.105 mol %) 4-N,N-dimethyl-benzaldehyde was added slowly; (5) When reaction (4) was finished, piperidine that plays a role of catalyst was added as droplets, and the color of the solution became red immediately; (6) The mixture of (5) was refluxed with the home-built Dean-Stark trap to remove the water. Then, the reactants were cooled to room temperature and the synthesized salt was collected; (7) The collected materials were dried in an oven at 100 ^{o}C for 1 h. Finally, the products were purified by recrystallization in methanol. Before film preparations, the products were systematically characterized by NMR, mass spectra, and element analysis, which results are shown in the following Figure S1, Figure S2, and Table S1. All data demonstrated that the as-synthesized products are DAST.

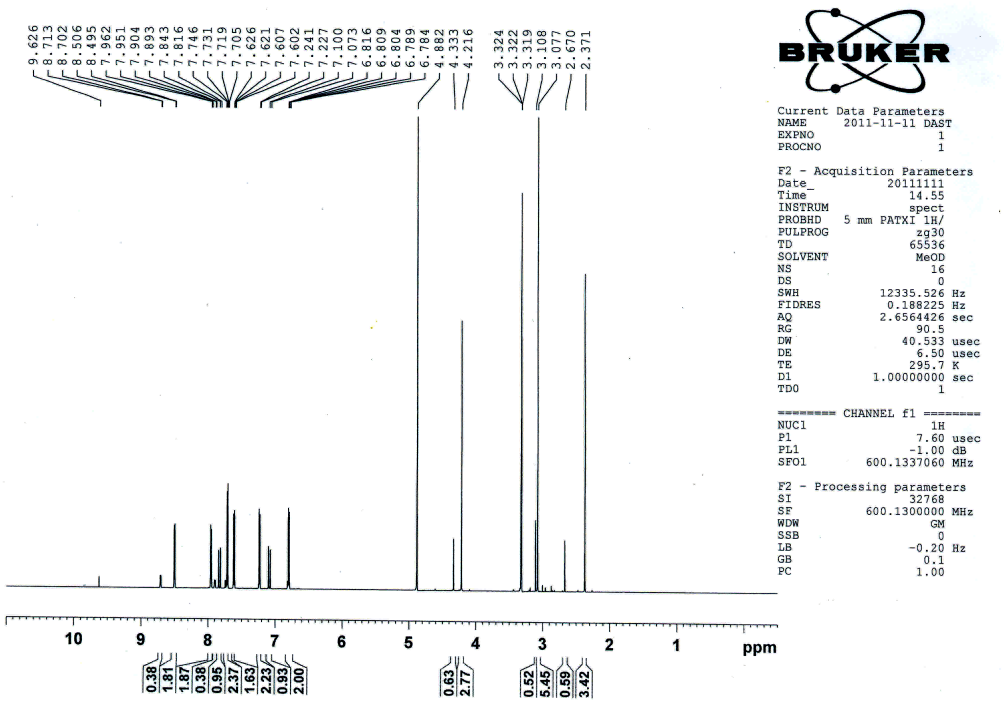
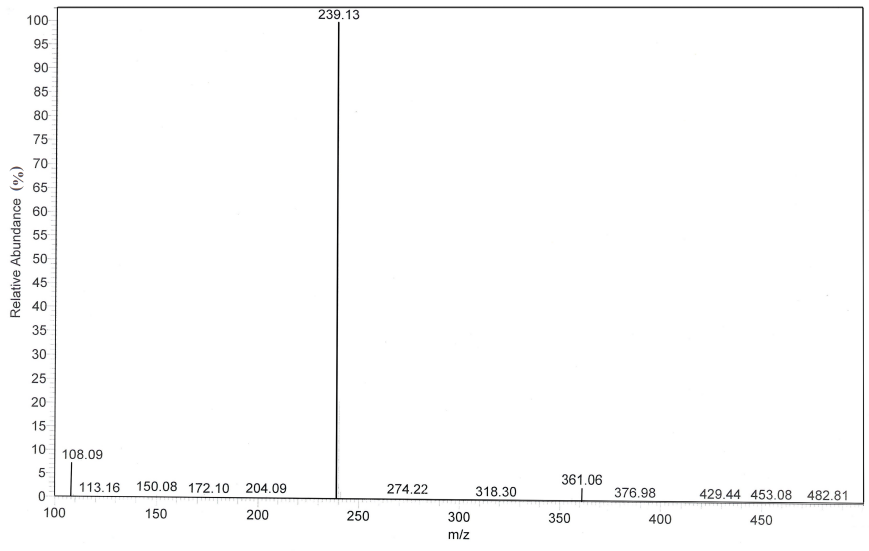
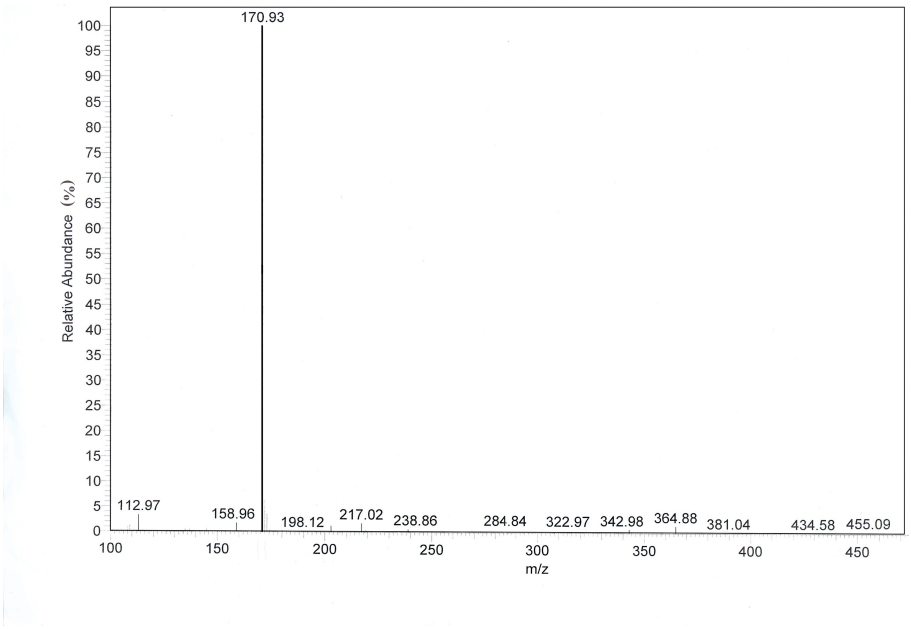


Figure S1. NMR result of the as-synthesized product.



(a)



(b)

Figure S2. Mass Spectra of of the as-synthesized product: (a) cation of DAST ($C_{16}H_{19}N_2^+$, measured mass of 239.13 *vs.* calculated mass of 239.34), and (b) anion of DAST ($C_7H_7SO_3^-$, measured mass of 170.93 *vs.* calculated mass of 171.19).

Table S1. Element Analysis of the as-synthesized product:

Elements	C	H	N	S
Measured	66.04%	7.06%	6.27%	7.54%
Calculated	67.29%	6.38%	6.82%	7.81%

2. Substrate pre-treatment:

Before film depositions, the substrates were treated through the following process: (1) Glass or Si(100) wafers were used as the deposition substrates, which were first

cleaned ultrasonically in acetone for 10 min, and then in ethanol for 10 min; (2) The substrates were then cleaned by ultrasonic bath for 10 min in a mixture of concentrated H_2SO_4 (28 mL) and H_2O_2 (12 mL); (3) The substrates were chemically cleaned again in a mixture of D.I. H_2O, NH_3 and H_2O_2 with a volume of 5:1:1 at 70 ^oC for 1h; (4) Finally, the substrates were rinsed with D.I. H_2O, and then they were dried by N_2 gas. Numerous experiments revealed that the DAST-based thin films prepared on unclean or cleaned hydrophobic substrate surfaces are rough, non-uniform, and knitted. In contrast, the DAST-based thin films prepared on cleaned hydrophilic substrates that have been pre-treated through above process are uniform and flat.

3. Film preparation:

The process for the preparation of high-quality nanocomposite films includes: (1) DAST that has been synthesized through 1 was dissolved in methanol to obtain a 0.008 wt.% DAST solution; (2) Using this DAST solution, the 1st DAST layer was spun coated onto a cleaned Si or glass substrate that has been pre-treated through 2, and then the residual solvent was removed by annealing at 50 ^oC. The optimal spin coating parameters include: first rotation at 500r/min for 5 seconds, and then at 3000r/min for 55 seconds; (3) Functionalized multi-walled carbon nanotubes (MWCNTs) were distributed in D.I. H_2O, and the 1st MWCNT layer was deposited onto the DAST surface by spray coating, and then annealing at 50 ^oC. The optimal

spray coating parameters include: high-purity N_2 as the carry gas with a pressure of 0.2 MPa, spraying nozzle with a size of 0.3 mm, keeping a distance of 10 cm between the nozzle and substrate, 0.2 wt.% CNT; (4) The 2nd DAST layer was deposited by spin coating under the similar parameters, and then annealing at 50 ^{o}C; (5) The 2nd MWCNT layer was deposited similarly by spray coating, then annealing at 50 ^{o}C; (6) Finally, the 3rd DAST layer was deposited similarly again by spin coating, then annealing at 50 ^{o}C. According to above procedures, the DAST-MWCNT composite films with MWCNT concentration ranging from 1.0 to 26.3 wt% were successfully prepared on Si and glass substrates. In contrast, the pristine DAST films were prepared on Si and glass substrates by spin coating of DAST for five times. Notably, the DAST films will be rough and non-uniform if spray coating is used for DAST deposition; and numerous CNTs are difficult to be dispersed uniformly by spin coating, and thus large loading of CNTs is troubled to be yielded by the spin method. That is to say, the film quality strongly depends on the preparation method and conditions. Under the optimal conditions and suitably combining spin coating and spray coating, namely the former for DAST deposition while the latter for CNT deposition, large-area uniform DAST-CNT composite films with device quality can be successfully prepared by these simple and conventional coating techniques.

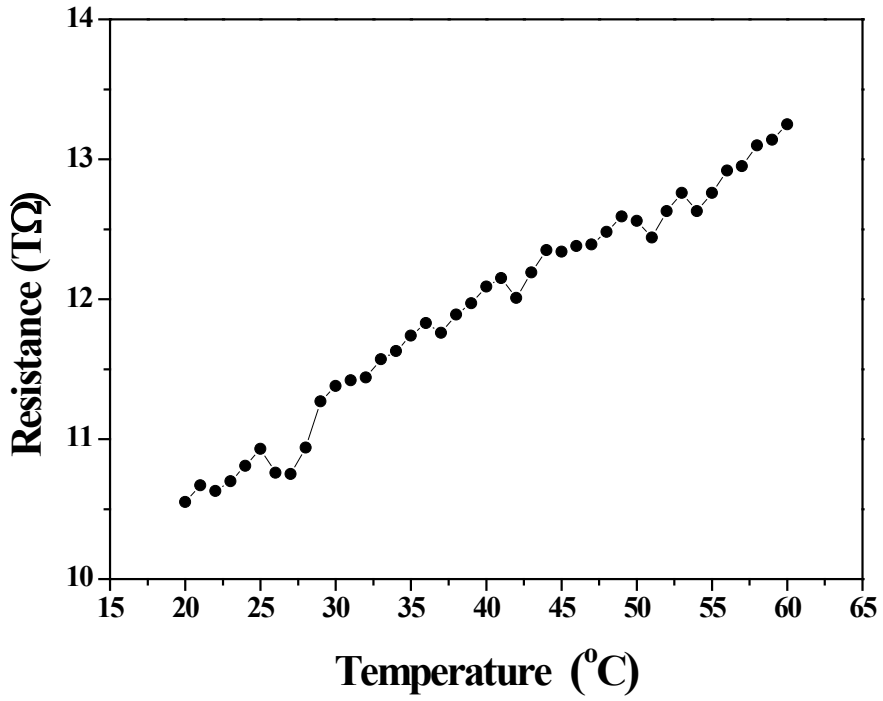
4. Electrodes preparation:

Our experiments have demonstrated that both magnesium silver (MgAg) and nickel

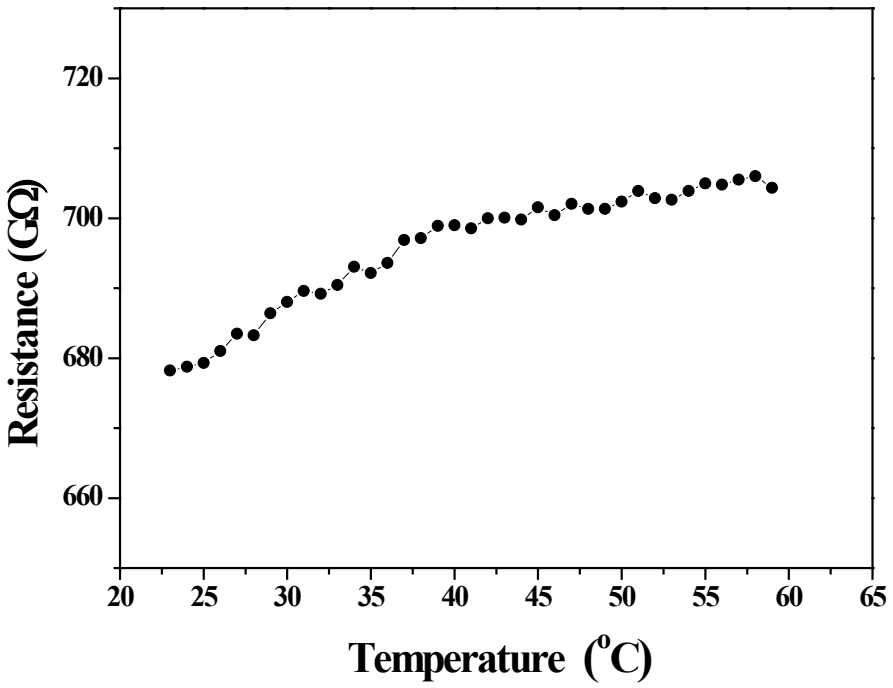
chromium (NiCr) can be utilized as electrodes for measuring the electrical properties of the resulting DAST-based films. The electrical data presented in this article were measured using MgAg electrodes. Such MgAg electrodes were deposited on the films by pattern deposition through thermal evaporation (SYUHVTI OLED-V) under the optimized conditions of: evaporation of Mg at 24 A, evaporation of Ag at 30 A, pressure of 3×10^{-3} Pa, Mg:Ag=10:1, film thickness of 150 nm, glass substrates. Two samples after deposition of electrodes on DAST and composite films are displayed following (Figure S3). Finally, the as-prepared samples were measured by high resistance meter (KEITHLEY 6517A).

Figure S3. Samples after deposition of electrodes on a DAST film (Left), and a composite film (Right).

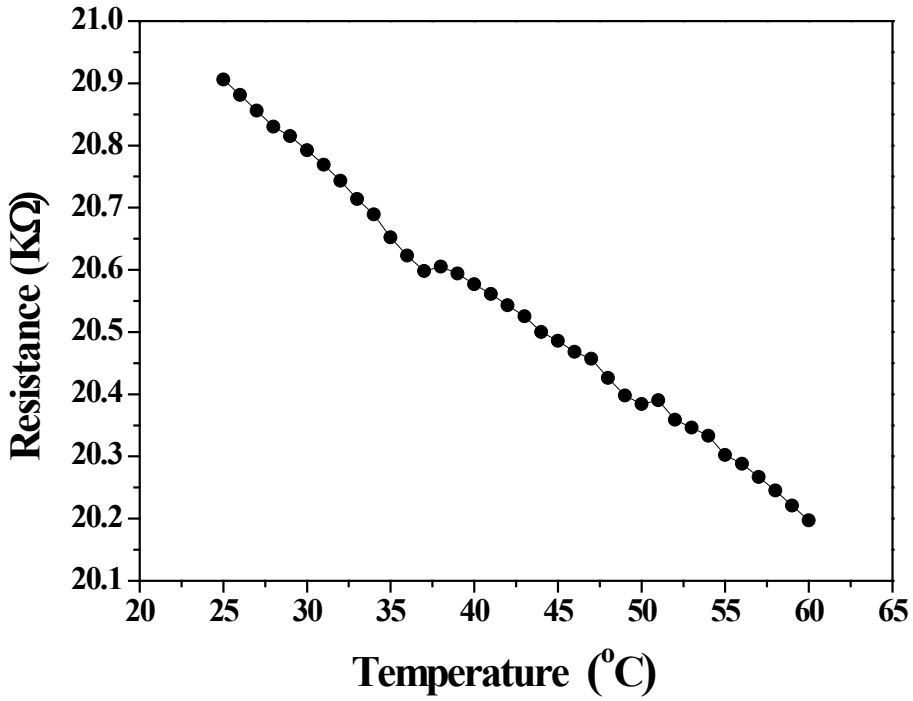
5. Sheet resistances for various films at different temperatures:



(a) Pristine DAST film (a positive *TCR*)



(b) DAST-1% CNT composite film (a positive *TCR*)



(c) DAST-6.7% CNT composite film (a negative *TCR*)

Figure S4. Sheet resistances of DAST and composite films at various temperatures.

In Figure S4a and 4b, the sheet resistance (*R*) increases with the increase of temperature, suggesting positive *TCR* in these two cases, as discussed in the text. In contrast, negative *TCR*, in which *R* decreases with the increase of temperature, is observed in Figure S4c. Similarly, negative *TCR* were obtained if the CNT concentration in the composite was higher than 6.7 wt%.