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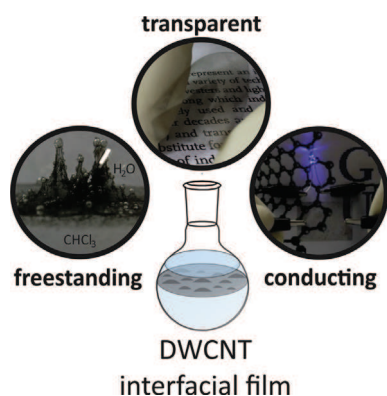
Conducting, transparent and flexible substrates obtained from interfacial thin films of double-walled carbon nanotubes

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GRAPHICAL ABSTRACT



ABSTRACT

Conducting and transparent interfacial thin films have been prepared from double-walled carbon nanotubes (DWCNT) and further deposited over glass and plastic (polyethylene terephthalate-PET) substrates. The morphology, vibrational structure as well as the optical and electrical properties have been evaluated. The influence of the DWCNT purifying treatment, the amount of carbon nanotubes used to prepare the thin films, and the annealing of the films at different temperatures has been evaluated to optimize both electrical and optical properties. Values of sheet resistance ranging from 0.53 to 27.8 $\text{k}\Omega \square^{-1}$ and transmittance at 550 nm from 59 to 90% have been achieved. Similar behavior obtained for films deposited on PET or glass substrates indicate a good reproducibility of the method, besides the high potential for further applications on flexible devices.

Keywords:

Transparent and flexible electrodes
ITO-replacement
Double-walled carbon nanotubes
Thin films
Liquid/liquid interfaces

1. Introduction

The development of conducting and transparent substrates (CTS's) has received a huge attention from researchers since this

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material plays important role as a component on the manufacturing of optoelectronic devices, such as organic light emitting diodes, organic solar cells, touch panels, and so on [1]. Low electrical resistance and high optical transmittance are desirable properties for materials intended to be applied in this field.

Tin-doped indium oxide (ITO) is with no doubt the most common substrate applied as CTS due to its outstanding optical (around 90 % of transparency) and electrical (sheet resistance

ranging 10–25 $\Omega \square^{-1}$) properties [1,2]. Moreover, the expertise in control of doping level and thickness of ITO make this substrate even more attractive and marketplace unanimously for CTS applications [3]. However, the development of new technologies which employ CTS's claims for materials with properties beyond the high transparency and low electrical resistance like flexibility, weightlessness, low cost and easy processability. ITO presents several drawbacks to achieve these previous requirements: it easily cracks under bending, which prevents further application on flexible substrates; indium resources are becoming even scarcer and the market for CTS's is markedly expanding; high temperature and vacuum procedures are necessary for ITO deposition, which also increase the process cost and makes harder the deposition over plastic substrates [1,4–6]. In order to overcome the drawbacks associated to ITO, several materials have been developed as an alternative for further application as CTS's, such as carbon nanomaterials (carbon nanotubes and graphene), metal gratings and random metallic nanowires networks [1,3].

In which concerns the use of carbon nanostructures as CTS's, carbon nanotubes are very promising materials as an alternative for ITO, due to the high electrical conductivity and high mechanical strength, which allows further applications of carbon nanotubes films in flexible devices [7]. Conducting and transparent films of single-walled carbon nanotubes (SWCNT) have been developed with sheet resistance ranging on 30–500 $\Omega \square^{-1}$ and transmittance at 550 nm achieving 90% [8–10]. Double-walled carbon nanotubes (DWCNT) are composed of two concentric tubes and can be considered as a more promising material for CTS's compared to SWCNT due to the lower junction resistance as a result of the larger tube diameter while keeping the good conductivity [11]. Few works have been reported preparing CTS's from DWCNT, which achieved good values of sheet resistance and transparency [11–13].

The processability of the active material as thin and transferable films is one of the most important steps for CTS's production. Several approaches have been reported for deposition of carbon nanotubes as thin films including filtration transfer, air-brushing, dip coating, drop casting, and so on [8,9,14,15]. Nevertheless, several drawbacks associated to the carbon nanotubes deposition as non-homogeneity and post multi-steps are usually required, preventing the thin and transparent film to be deposit directly over the desired substrate.

The production of thin, transparent and freestanding films assembled at the interface of two immiscible liquids in a single step has been an outstanding method to prepare films with high homogeneity, controllable thickness and with a variety of applications [16–18]. The interfacial route is a very simple way to prepare thin films in a single step, under environment conditions and easily transferable to different kind of ordinary substrates, including plastics [16,17]. CTS's from different carbon nanostructures assembled at the liquid-liquid interface have been prepared, where sheet resistance ranging 1.7–50 $k\Omega \square^{-1}$ and transmittance up to 85% at 550 nm were achieved [19]. Films were also deposited over flexible substrates (PET) and high stability of sheet resistance was achieved even after several bending cycles.

In the presented study, thin and transparent films of DWCNT processed using different treatments have been prepared through the interfacial method for further application as CTS's. The values of sheet resistance and transparency have been correlated to the morphology of the films and the structure of the DWCNT. The relation between the purification treatments, the amount of DWCNT and the annealing process of the thin films has been studied. The interfacial thin films were also deposited over flexible substrates to enable further application on flexible optoelectronic devices.

2. Experimental

DWCNT's synthesis and all post-purifying procedures applied to carbon nanotubes were previously described elsewhere [20,21]. Interfacial thin films of DWCNT's were produced following similar method already reported for SWCNT's and graphene [19,22]. It is noteworthy that the DWCNT's dispersions were prepared using two different solvents (deionized water or chloroform) depending on the purification treatment applied to the carbon nanotubes. Samples were named after the purifying treatment adopted.

2.1. DWCNT's purifying treatment

Briefly, all the samples investigated in this work were prepared from the same batch of raw DWCNT. Air/HCl treatment consisted in heating the sample for 30 min in air at 500 °C and washing it with aqueous solution of HCl 12 mol L⁻¹ overnight at room temperature. HNO₃ oxidation was performed at 130 °C for 24 h in 3 mol L⁻¹ of nitric acid followed by washing with either only water (H₂O), or water followed by sodium hydroxide aqueous solution (4 mol L⁻¹) at 130 °C for 24 h (NaOH). HNO₃/H₂SO₄ processing consisted in refluxing the DWCNT in a HNO₃/H₂SO₄ (1:3) aqueous solution at 130 °C for 5 h, followed by washing with either water (H₂O), or water/sodium hydroxide aqueous solution as described before.

2.2. DWCNT's interfacial thin films

Table 1 summarizes the solvent and conditions used to prepare the DWCNT's dispersion.

The steps adopted to produce interfacial thin films are described as follow: a given amount of DWCNT was added into a beaker containing 32 mL of solvent (Table 1). The mixture was maintained under sonication using an ultrasonic probe system (Cole Palmer ultrasonic processor with 40% of amplitude and interval time of 59" on and 10" off), to obtain a stable dispersion. The DWCNT's dispersion with no visible flocculate was transferred into a round bottom flask containing 20 mL of the solvent to form the interfacial system (chloroform in the case of DWCNT dispersion in deionized water or deionized water in the case of DWCNT dispersion in chloroform). The interfacial system was maintained under magnetic stirring at 2500 rpm for 3 h. A thin and transparent film could be noticed, assembled at the liquid-liquid interface when the magnetic stirring was interrupted. Chloroform was removed and exchanged by toluene to keep the organic solvent on the top. The interfacial thin film was transferred with the aid of a pipette to a beaker containing the interfacial system (toluene/deionized water) and the substrates assembled on the bottom of the flask. The interfacial thin films were deposited on different substrates, removed from the bottom of the beaker with the aid of tweezers. Films were dried at 70 °C for 1 h in air. The schematic representation of all steps involved in the experimental

Table 1
Summary of the setup used to prepare the interfacial thin films for each sample.

Sample	Solvent	Amount of DWCNT (mg)	Sonication time
raw DWCNT	CHCl ₃	0.2	20 min
DWCNT-Air/HCl	CHCl ₃	0.05/0.1/0.2	20 min
DWCNT-HNO ₃ (H ₂ O)	H ₂ O	0.2	30 min
DWCNT-HNO ₃ (NaOH)	H ₂ O	0.2	30 min
DWCNT-HNO ₃ /H ₂ SO ₄ (H ₂ O)	H ₂ O	0.05/0.1/0.2	60 min
DWCNT-HNO ₃ /H ₂ SO ₄ (NaOH)	H ₂ O	0.2	60 min

atmosphere was also performed. Films deposited over glass substrates were placed into the oven and heated to the desired temperature for 2 h using a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in flowing air.

2.4. Characterizations measurements

DWCNT's interfacial thin films morphology on silicon substrates was evaluated using scanning electron microscopy (SEM-FEM/Tescan). Raman spectra of the films on silicon substrates were recorded using a Renishaw Raman image spectrophotometer with excitation line of 1.96 eV (632.8 nm/He-Ne laser). The transmittance of the films over quartz substrates was acquired using a Shimadzu UV-2450 spectrophotometer. Sheet resistance (SR) and thickness of DWCNT interfacial thin films were recorded on glass substrates. SR was determined through the four-point method using a Jandel Universal probe equipment. The thickness of the films was measured using a Dektak 150 Veeco profilometer with a resolution and probe strength of $0.010\text{ }\mu\text{m}$ and 1 mg, respectively.

3. Results and discussion

The technique to assemble dispersible materials on the interface of two immiscible solvents as thin, transparent, and freestanding films has shown to be an outstanding method to prepare films capable to be deposited over different substrates with diverse applications [16–18]. As can be noticed in the digital image presented in the middle of Fig. 1, transparent and macroscopically homogeneous films on glass substrates were produced from DWCNT samples.

Fig. 2 shows the SEM images for the different samples of interfacial thin films of DWCNT (0.2 mg) directly deposited from the interface on silicon substrates. Through the images of raw DWCNT in Fig. 2 (a) and (b) the presence of large agglomerates of DWCNT as well as few carbon nanotubes randomly distributed over the substrate is clearly visible. The presence of these large agglomerates (also called “diaphanous carbon”) is resulting from CCVD synthesis of DWCNT and keeps the carbon nanotubes entangled [21]. The morphology of DWCNT-Air/HCl in Fig. 2(c) and (d) is totally different from raw DWCNT sample and no diaphanous carbon could be noticed. The presence of many entangled nanotubes in DWCNT-Air/HCl comparing with images of raw DWCNT at the same magnification is notorious. The simple annealing of the

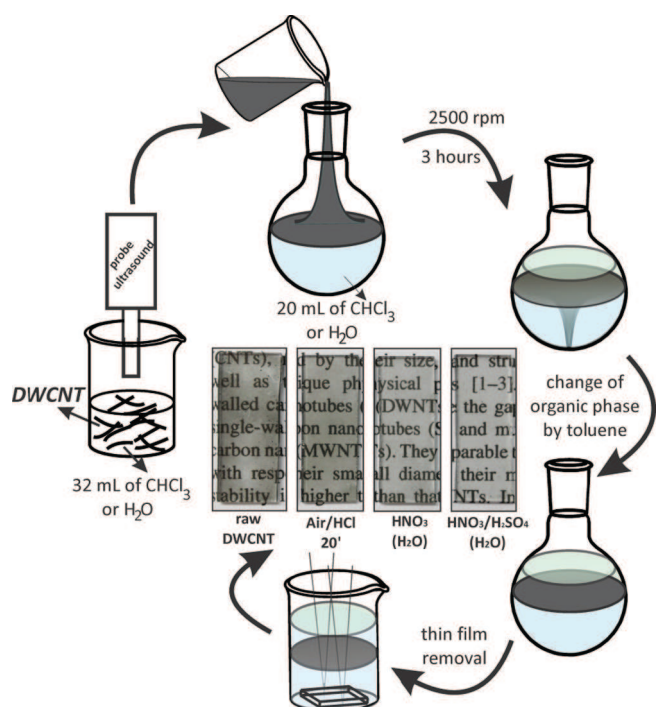


Fig. 1. Schematic representation of all steps involved in interfacial films production and photographic image (in the middle) of DWCNT's films deposited over glass substrate.

procedure is shown in Fig. 1. The transparency and optical quality of the films obtained can be seen in the photograph image also presented in the middle of Fig. 1.

DWCNT-Air/HCl and DWCNT-HNO₃/H₂SO₄ (H₂O) films were also prepared using three different initial amounts of carbon nanotubes (0.05, 0.1 and 0.2 mg). For all other samples, films were prepared only using 0.2 mg of DWCNT.

2.3. DWCNT's thermal annealing

Thermal annealing of DWCNT-Air/HCl and DWCNT-HNO₃/H₂SO₄ (H₂O) samples at 200, 300 and 400 °C under oxidizing

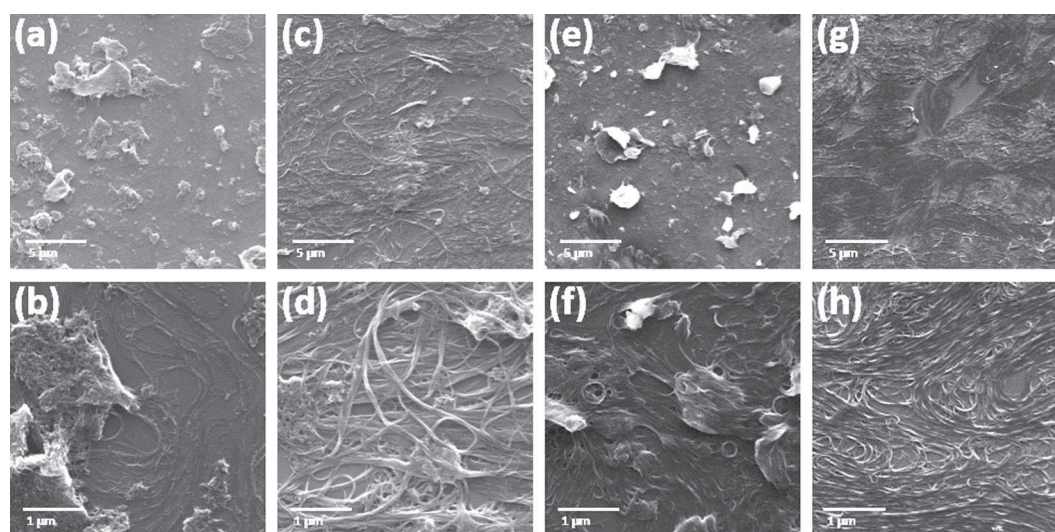


Fig. 2. SEM images of the films deposited over silicon substrates: raw DWCNT (a and b), DWCNT-Air/HCl (c and d), DWCNT-HNO₃ (H₂O) (e and f) and DWCNT-HNO₃/H₂SO₄ (H₂O) (g and h).

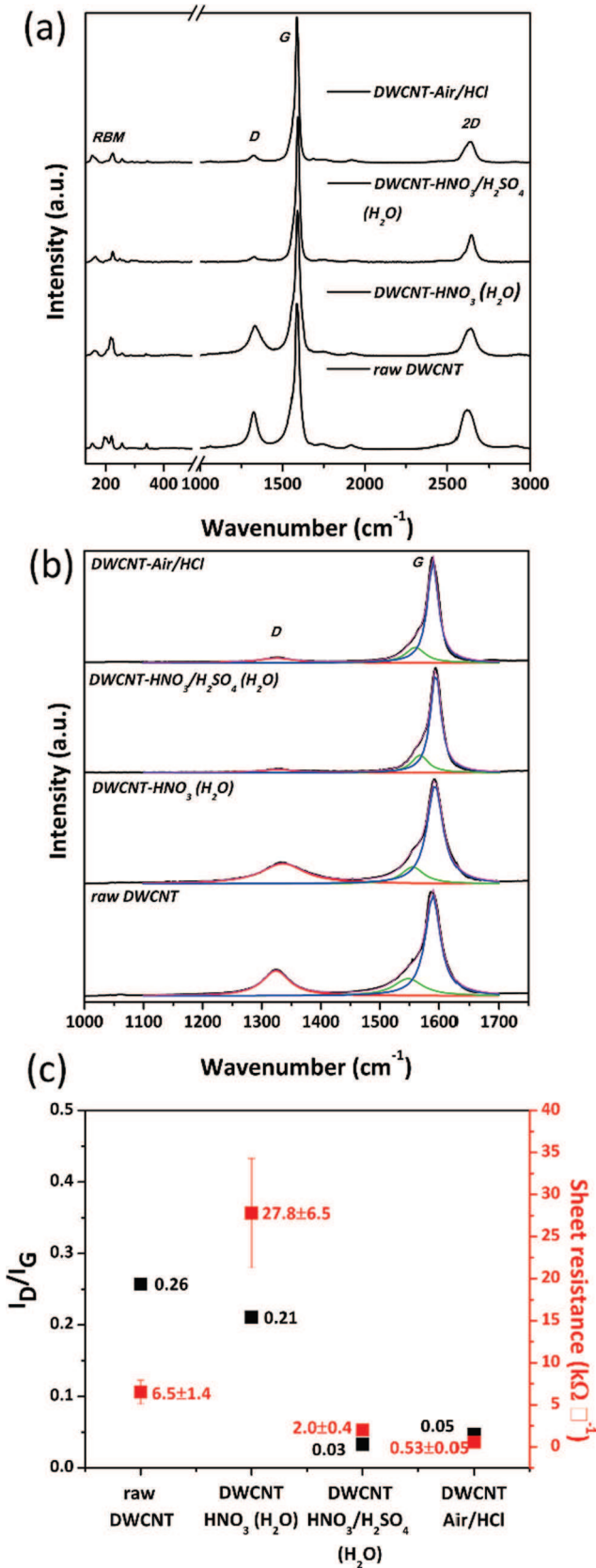


Fig. 3. Raman spectra of DWCNT thin films (a); detail from 1000 to 1750 cm⁻¹ with the deconvolution of peaks (b); correlation between I_D/I_G ratio and sheet resistance of the different DWCNT films (c). Black full squares refer to I_D/I_G values and red full square refer to sheet resistance.

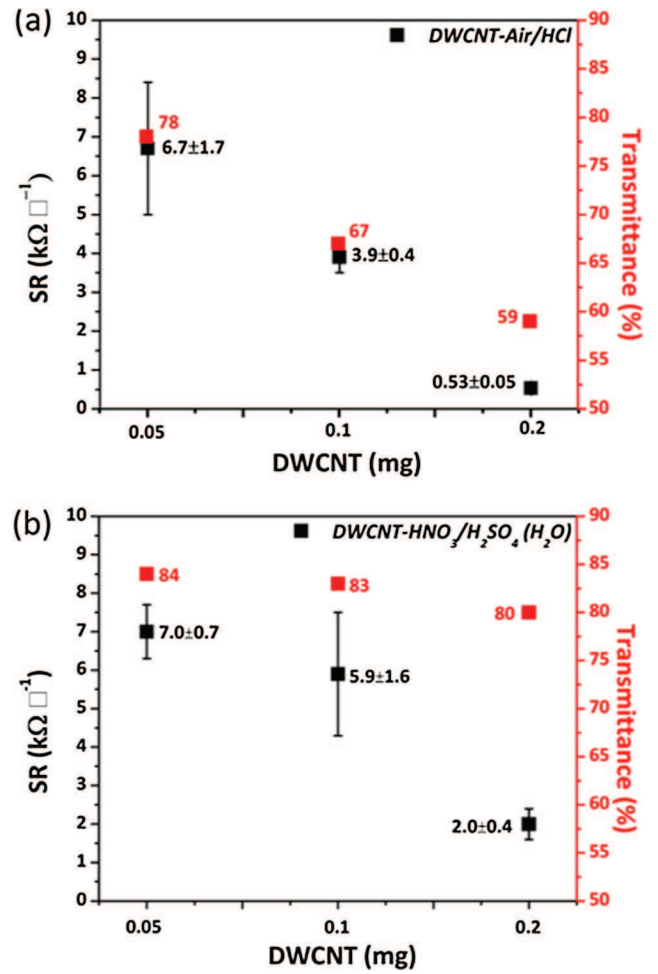


Fig. 4. Sheet resistance and transmittance at 550 nm vs DWCNT amount for Air/HCl (a) and HNO₃/H₂SO₄(H₂O), (b) films. Black full squares refer to sheet resistance and red full squares refer to transmittance.

DWCNT followed by washing with HCl is quite enough to remove oxide and residual catalyst without damaging the DWCNT surface [21,23,24]. For DWCNT-HNO₃(H₂O) sample in Fig. 2 (e) and (f), some entangled DWCNT agglomerates are still present, as also observed for DWCNT-HNO₃(NaOH) sample (Fig. S1(a) and (b)). No agglomerates can be noticed for DWCNT-HNO₃/H₂SO₄(H₂O) sample in Fig. 2(g) and (h) as well as for DWCNT-HNO₃/H₂SO₄(NaOH) in Fig. S1(c) and (d), indicating here a good condition to remove the diaphanous carbon from DWCNT, resulting in better homogeneity in the film morphology.

Raman spectra from different samples of DWCNT interfacial thin films are shown in Fig. 3(a). The presence of the main peaks concerning DWCNT can be noticed in Fig. 3(a), with the radial breathing modes (RBM) at low frequency region; D band around 1324 cm⁻¹, attributed to the presence of defects in the carbon nanotube structure; the G band split in G⁻ and G⁺ at 1560 and 1590 cm⁻¹, corresponding to circumferential and longitudinal carbon atoms vibration; and the 2D band at 2640 cm⁻¹, which is an overtone of the D band [23,25]. DWCNT-HNO₃(NaOH) and DWCNT-HNO₃/H₂SO₄(NaOH) exhibited very similar Raman spectra profiles for the respective samples washed with H₂O (Fig. S2 (a)). As described previously, the I_D/I_G ratio is an important parameter to quantify the level of defects in the carbon nanostructure, and a large I_D/I_G ratio is normally related to a high level of defects on the surface of the carbon nanostructure [24,26]. Fig. 3(b) depicts

a detail of Fig. 3(a) from 1000 to 1750 cm^{-1} , as well as the deconvolution for each peak. The I_D/I_G ratio for raw DWCNT was 0.26, while for DWCNT-Air/HCl sample, the I_D/I_G ratio dropped down to 0.05, indicating much less defects in the carbon nanotube structure. An increase in I_D/I_G ratio was noticed for DWCNT- HNO_3 (H_2O), with a value of 0.21. Similarly, the sample washed with NaOH also presented an increased I_D/I_G ratio (Fig. S2(b)), with a value of 0.18. This behavior was already attributed to a preferential oxidation of diaphanous carbon, leading to CCF's formation [21]. Both DWCNT- $\text{HNO}_3/\text{H}_2\text{SO}_4$ (H_2O) and (NaOH-Fig. S2(b)) presented a decrease in I_D/I_G ratio, analogous to the DWCNT-Air/HCl sample, with values of 0.03 and 0.05, respectively. Fig. 3(c) shows I_D/I_G ratios in association to the values of sheet resistance (SR) of the thin films. As expected, the lowest values of SR were achieved for the samples with low I_D/I_G ratios (Air/HCl and $\text{HNO}_3/\text{H}_2\text{SO}_4$ (H_2O)), indicating a sp^2 network which allows a better electronic transport. It can be noticed that the lower values of I_D/I_G as well as of SR were achieved for samples which resulted in films with more homogeneous morphology, as observed through the SEM images. Surprisingly, the DWCNT- HNO_3 (H_2O) sample presented higher SR value even when compared to the raw DWCNT. This is in agreement with previous results which attributed a higher production of carboxylated carbonaceous fragments coating all outer DWCNT surface for samples purified with HNO_3 [21].

DWCNT-Air/HCl and $\text{HNO}_3/\text{H}_2\text{SO}_4$ (H_2O) samples presented the best results of SR compared to the other samples prepared in this work. From this point of view, further experiments were developed to optimize the values of SR, besides the transmittance at 550 nm. Fig. 4(a) and (b) depict the SR values and transmittance (%) at 550 nm for interfacial thin films prepared from three different amounts of DWCNT Air/HCl and $\text{HNO}_3/\text{H}_2\text{SO}_4$ (H_2O), respectively. As can be noticed in both graphics, the lowest SR values were obtained for DWCNT samples prepared from 0.2 mg of carbon nanotubes. On the other hand, the lower transmittance values were also achieved for these samples, with values of 59 and 80 % at 550 nm for DWCNT-Air/HCl and DWCNT- $\text{HNO}_3/\text{H}_2\text{SO}_4$ (H_2O), respectively. High transmittance was obtained for samples with a low amount of DWCNT (0.05 mg), with values of 78 and 84 % at 550 nm for Air/HCl and $\text{HNO}_3/\text{H}_2\text{SO}_4$ (H_2O) samples. The thickness of the DWCNT interfacial films also decreased when the amount of carbon nanotubes was lower, achieving 30.2 ± 7.9 and 14.8 ± 2.9 nm for DWCNT-Air/HCl and $\text{HNO}_3/\text{H}_2\text{SO}_4$ (H_2O) samples, respectively, for films prepared from 0.05 mg of carbon nanotubes (Fig. S3(a) and (b)). Nevertheless, the SR values increased for these samples, although the transmittance and thickness were optimized. This increase in SR should be due to the decrease in connectivity arising from the lower amount of carbon nanotubes in the film [27,28].

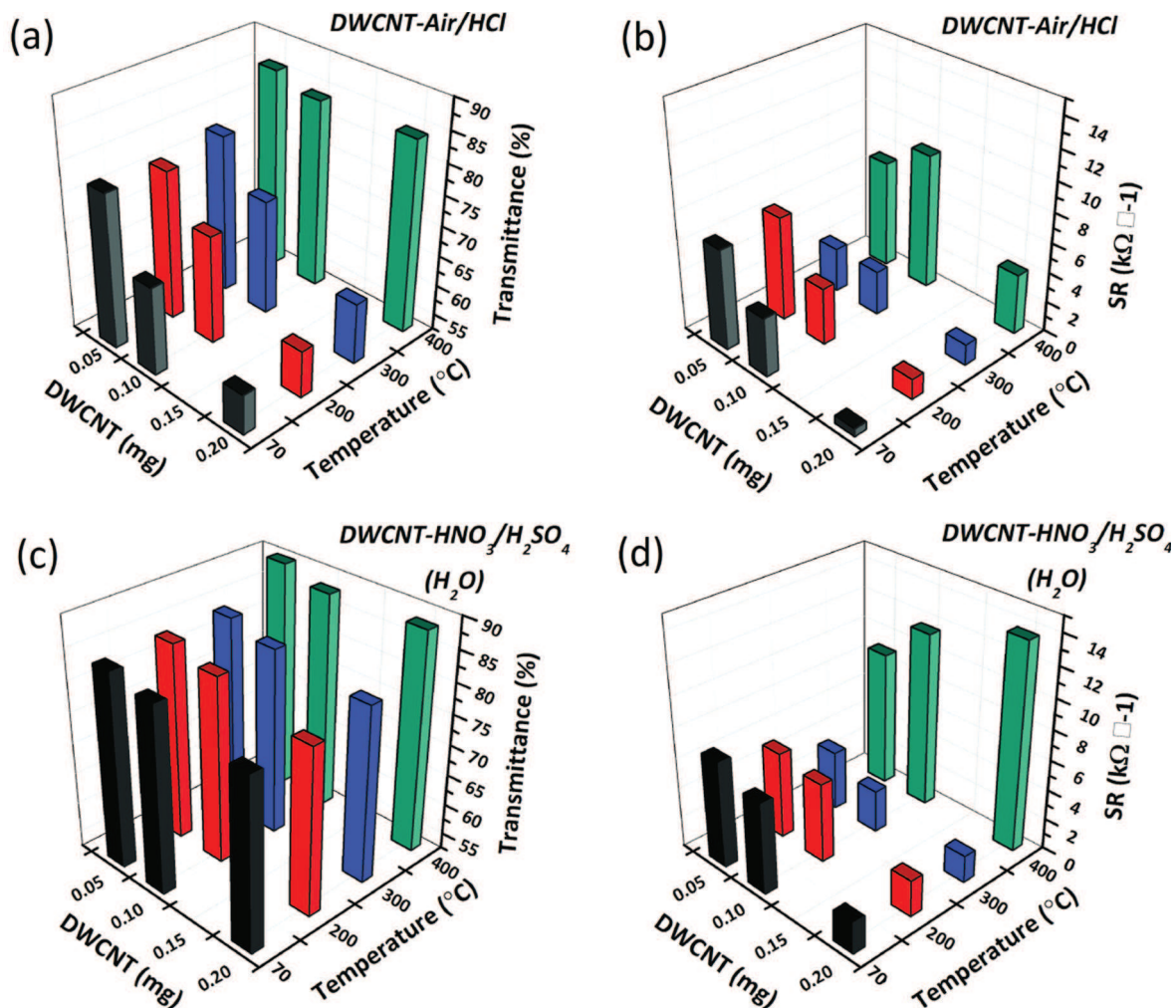


Fig. 5. Transmittance at 550 nm vs the amount of DWCNT and the temperature of annealing of the Air/HCl (a) and $\text{HNO}_3/\text{H}_2\text{SO}_4$ (H_2O) (c) films; sheet resistance vs the amount of DWCNT and the temperature of annealing of the Air/HCl (b) and $\text{HNO}_3/\text{H}_2\text{SO}_4$ (H_2O), (d) films.

Table 2Sheet resistance ($k\Omega \square^{-1}$) and transmittance (%) of the films vs both the amount of DWCNT and the annealing temperature.

	DWCNT-Air/HCl			DWCNT-HNO ₃ /H ₂ SO ₄ (H ₂ O)		
	0.05 mg	0.1 mg	0.2 mg	0.05 mg	0.1 mg	0.2 mg
70 °C	6.7 ± 1.7/78	3.9 ± 0.4/67	0.5 ± 0.1/59	7.0 ± 0.7/84	6.0 ± 1.6/83	2.0 ± 0.4/80
200 °C	6.9 ± 1.5/77	3.8 ± 0.5/70	0.9 ± 0.1/68	5.7 ± 0.7/84	5.2 ± 1.2/83	2.4 ± 0.3/80
300 °C	3.0 ± 0.9/79	3.0 ± 0.4/72	1.1 ± 0.3/69	3.9 ± 0.6/85	2.8 ± 0.4/83	1.8 ± 0.3/81
400 °C	7.2 ± 0.8/86	9.1 ± 0.8/84	1.7 ± 0.1/78	9.0 ± 1.6/90	11.6 ± 2.8/88	13.7 ± 3.1/88

DWCNT-Air/HCl and HNO₃/H₂SO₄ (H₂O) films were annealed under oxidizing atmosphere at three different temperatures (200, 300 and 400 °C) to optimize the SR and transmittance values. Annealing process is known to improve SR and transmittance values of thin films prepared from different carbon nanostructures since this procedure removes carbon impurities, decreases the tube-tube junction resistance, and restores the sp² structure on the carbon nanostructures. [5,29,30] Fig. 5 presents SR and transmittance values obtained for each temperature, depending on the amount of carbon nanotube used to prepare the interfacial films. Table 2 summarizes all values obtained of SR and transmittance for each temperature. The improvement of the transmittance with the increase in temperature is very clear. The transmittance at 550 nm increased for all samples from 200 to 400 °C. The highest values of transmittance (Fig. 5 (a) and (c)) were achieved for samples prepared from 0.05 mg of DWCNT and annealed at 400 °C, being 86 and 90% for DWCNT-Air/HCl and HNO₃/H₂SO₄ (H₂O), respectively. Even though some improvement was achieved on values of transmittance of the thin films, the changes in terms of SR were not so meaningful.

The SR slightly increased after annealing for DWCNT-Air/HCl sample prepared with 0.2 mg, achieving values twice higher at 400 °C (Fig. 5(b)). The thin films prepared with 0.1 and 0.05 mg presented significant decrease in SR until 300 °C, which become higher after annealing the DWCNT samples at 400 °C. Similar behavior could be noticed for all DWCNT-HNO₃/H₂SO₄ (H₂O) samples (Fig. 5(d)), which exhibited low SR values for films annealed at 300 °C. The decrease in SR for almost all films from 70 °C to 300 °C can be associated to removing some impurities, as amorphous carbon for example, or even through restoring the C-C sp² bonds in the DWCNT from the decomposition of functional groups [19]. The SR value for all films increased when the annealing temperature was increased to 400 °C. This behavior can be attributed to the oxidation of carbon nanotubes, or at least some of them leading to both a lower number of remaining carbon nanotubes, and fewer interconnections. In the case of the DWCNT-Air/HCl sample the explanation may be more complex as the nanotubes already experienced an oxidizing treatment at a temperature much higher than 400 °C (500 °C), but only for 30 min compared to the 2 h of the heat treatment discussed here. It is thus possible that some carbon nanotubes were burnt during this step.

As mentioned before, besides the capacity to develop conducting and transparent films, new technologies claim for materials capable to be assembled over flexible substrates standing the electrical and optical properties even under mechanical stress (as under stretching or bending, for example). To prove this capability, interfacial thin films of DWCNT-Air/HCl and DWCNT-HNO₃/H₂SO₄ (H₂O) produced from 0.2 mg of carbon nanotubes were deposited over flexible substrates of PET. A transparent and homogeneous film of DWCNT-Air/HCl on the flexible substrate can be observed in Fig. 6 (a), which presented excellent adherence to the substrate and no macroscopic damage under bending (Fig. 6(b)). Reasonable values of SR and transmittance at 550 nm (Fig. 6(c)) were achieved for both DWCNT samples deposited on PET when compared to the same samples on glass substrates, indicating the maintenance of

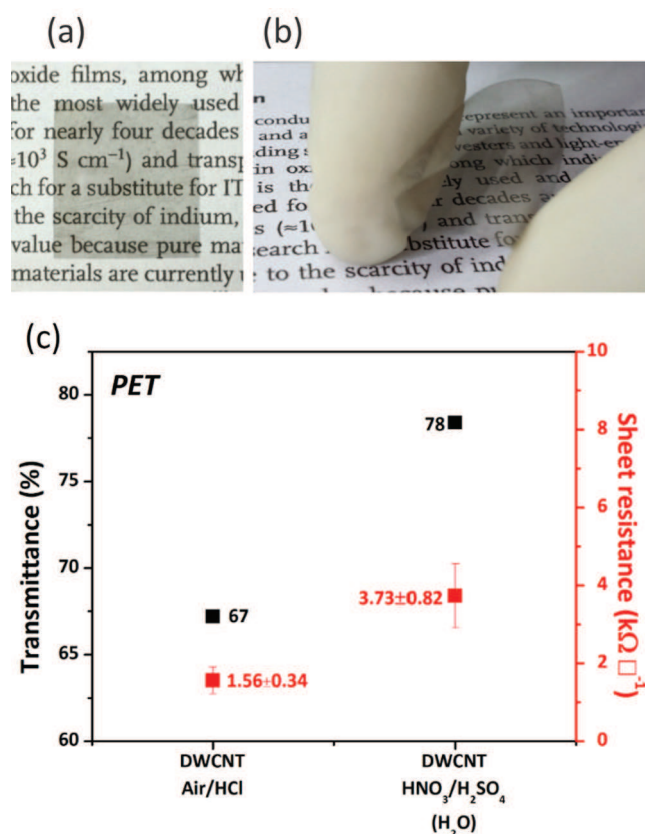


Fig. 6. Photographic images of the DWCNT Air/HCl film deposit on PET at rest (a) and under bending (b); transmittance at 550 nm and sheet resistance of the Air/HCl and HNO₃/H₂SO₄ (H₂O) films on PET (c). Black full squares refer to transmittance and red full squares refer to sheet resistance.

electronic and optical properties. Both samples on the flexible substrate were also applied as conducting substrate to close a circuit between a LED and a battery (video Supp. Inf), and it could be observed that both substrates worked well even under bending, indicating a promising viability for further applications in electronics devices.

The best results regarding SR and transmittance for conducting and transparent substrates in this work were achieved from the DWCNT-Air/HCl interfacial thin films. As described before, the lowest SR value was $0.5 \pm 0.1 k\Omega \square^{-1}$ with transmittance at 550 nm of 59%, whereas the highest transmittance was 78%, followed by a SR of $1.7 \pm 0.1 k\Omega \square^{-1}$. The optoelectronic performance of these films is quite compatible with some results described elsewhere, like for DWCNT thin films obtained from a layer-by-layer assembly ($0.413 k\Omega \square^{-1}$ and 87 % transmittance) [12]; for DWCNT films prepared from vacuum filtration and transferred to glass substrates ($0.146 k\Omega \square^{-1}$ and 75 % transmittance) [13]; for urea-functionalized SWCNT rolled films ($1.7 k\Omega \square^{-1}$ and 80 % transmittance) [31]; and for DWCNT film obtained from filtration ($0.083 k\Omega$

\square^{-1} and 79 % transmittance) [11]; The main breakthrough of this work is the production of conducting and transparent films of high structural quality DWCNT's assembled at the liquid-liquid interface, which are capable to be deposited over different substrates. Furthermore, the optoelectronic properties of these films can be easily tuned up only through the amount of DWCNT, and no complex post-step processing is required from the interfacial method for thin films production. So, the simplicity allied to the reproducibility of this method brings a contribution to the field of conducting and transparent substrates.

4. Conclusions

Conducting and transparent substrates obtained from thin films of double-walled carbon nanotubes assembled at a liquid-liquid interface were demonstrated here, which is an easy, cheap, and reproducible method to prepare thin films. Different approaches for DWCNT dispersions and further preparation of the interfacial thin films were strictly related to the purification treatment previously applied to the carbon nanotubes. Films were deposited on glass or PET substrates, and the morphology, the vibrational structure as well as the optical and electrical properties of these films were also evaluated. Samples prepared from DWCNT-Air/HCl and DWCNT-HNO₃/H₂SO₄ (H₂O) demonstrated the best electrical result. It was related to thin films with well-distributed carbon nanotubes on the substrates without the presence of entangled portions, combined to carbon nanotubes of very high structural quality (low I_D/I_G ratio). We demonstrated that the sheet resistance and the optical transparency of these two samples can be controlled through the amount of DWCNT and annealing process, which allows the modulation of the properties of the thin films depending on the future applications. The capability to prepare conducting and transparent films on plastic substrates allows these materials to be applied in fields where flexibility is required, which is impossible with ITO.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2017.04.084>.

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