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Work function engineering of ZnO electrodes by using p-type and n-type doped carbon nanotubes

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Abstract
Transparent electrodes in organic electronic devices are strongly needed in order to replace indium tin oxide (ITO). Some of the best candidates are ZnO films, which have shown both good electronic properties and solution processability compatible with roll-to-roll production of the devices. We present the possibility to engineer the work function of ZnO by blending it with carbon nanotubes (CNTs). B-doped (p-type), N-doped (n-type) and undoped CNTs as well as their blends with ZnO have been characterized by atomic force microscopy (AFM), scanning Kelvin probe microscopy (SKPM) and Raman spectroscopy. The results of Raman spectroscopy demonstrate the substitutional doping of carbon nanotubes, which preserves their covalent structure although increasing the disorder within the nanotubes. The roughness and average shape of grains of ZnO when blended with the doped nanotubes have been measured by AFM. Finally, SKPM shows that the work function of the blends can be engineered from 4.4 ± 0.1 to 4.9 ± 0.1 eV according to the kind of nanotube that is blended even if only a small amount of nanotubes is added to the blend (0.08 wt%).

Online supplementary data available from stacks.iop.org/Nano/24/484013/mmedia
(Some figures may appear in colour only in the online journal)

1. Introduction
Emerging photovoltaic technologies are predicted to meet grid parity costs for electricity production in the coming years [1]. One of the roadmaps for achieving this ambitious task is the search for a polymeric photovoltaic device (or ‘plastic solar cell’ [2]) that can be fabricated by a continuous roll-to-roll processing method from solution, which will significantly reduce the economic cost and the environmental impact of the manufacturing process [3]. Life cycle analysis of the manufacturing process of such devices, which also includes a detailed material inventory and the energy inputs associated to each material, has pointed to indium tin oxide (ITO) as one of the bottlenecks for the future production of low embedded energy and low cost solar cells [4]. It is therefore necessary to look for alternative transparent conducting electrodes for organic solar cells [5] (and other optoelectronic devices, such as OLEDs and phototransistors).

In recent years, ZnO has seen a revival in its technological interest. This semiconducting material has a wide band
than 140 based ideally on solution at processing temperatures lower of organic solar cells, ZnO production methods should be to be integrated in low temperature roll-to-roll processing including hybrid ZnO/metal nanostructures [15]. If ZnO is grown by chemical vapour deposition [15], tetrapods from nanofibres (electrospun mats at 450°C) inverted structures. mobility and the mismatch in energy levels for standard or (power conversion efficiency) is always lower than that of the achieved for small molecule solar cells [16], dye sensitized ratio for reliable flexibility on plastic substrates. This has been microcrystallinity) for good charge transport and a thin aspect potential for room temperature ballistic transport due to mentioned above. CNTs have been shown to have a large avoids the need for native defect control by irradiation as this problem by using mixtures of ZnO and carbon nanotubes (CNTs) and at the same time keep good crystallinity (or carbon nanotubes (CNTs) and (iii) ZnO blended kinds: (i) ZnO, (ii) B-doped (p-type), N-doped (n-type) or in detail in [35, 36]. They consist of thin films of three sample preparation and experimental details

The samples were prepared following procedures described in detail in [35, 36]. They consist of thin films of three kinds: (i) ZnO, (ii) B-doped (p-type), N-doped (n-type) or undoped carbon nanotubes (CNTs) and (iii) ZnO blended with a small amount of doped or undoped CNTs, all of them deposited on fluor-doped tin oxide (FTO) substrates by spray pyrolysis in a glove box. All samples were stored in inert atmosphere at room temperature (glove box); they were only in contact with air during measurements. The CNTs had substitutional doping of electron-deficient boron (B) or electron-rich nitrogen (N), which systematically altered the Fermi level position within the band gap of ZnO controlled by irradiation of samples is not compatible with inexpensive and fast manufacturing processes. Furthermore, the use of radiation damage to dope the samples is not compatible with most of the well-controlled growth mechanisms which nowadays yield most ZnO nanostructures: single crystal epitaxial films deposited by pulsed laser deposition [10], nanoparticle synthesis from MeOH solution [11], nanocoral fabricated on top of a Zn layer by radio-frequency magnetron sputtering followed by thermal oxidation at 500°C [12], nanofibres (electrospun mats at 450°C) [13], nanorods grown by chemical vapour deposition [15], tetrapods from 'powder' in ethanol solution [14], and many other approaches including hybrid ZnO/metal nanostructures [15]. If ZnO is to be integrated in low temperature roll-to-roll processing of organic solar cells, ZnO production methods should be based ideally on solution at processing temperatures lower than 140°C and at the same time keep good crystallinity (or microcrystallinity) for good charge transport and a thin aspect ratio for reliable flexibility on plastic substrates. This has been achieved for small molecule solar cells [16], dye sensitized solar cells [17], hybrid solar cells (using nanoparticle mixed with polymers in the active layer) [18, 19] and polymeric solar cells [20–24], but the performance of the devices (power conversion efficiency) is always lower than that of the benchmark device which uses ITO, mainly due to the lower mobility and the mismatch in energy levels for standard or inverted structures.

In all cases the problem of controlled doping of ZnO remains a challenge. Novel approaches have tried to overcome this problem by using mixtures of ZnO and carbon nanotubes (CNTs) as electrodes instead of bare ZnO. This strategy avoids the need for native defect control by irradiation as mentioned above. CNTs have been shown to have a large potential for room temperature ballistic transport due to quantization of charge in individual nanotubes, including both single wall carbon nanotubes (SWNTs) [25] and multiwall carbon nanotubes (MWNTs) [26]. However, device applications have been difficult to achieve mainly due to problems with charge transfer between nanotubes and to the subsequent electrode connection to the network of nanotubes. A mixture of ZnO and SWNTs has been used for the electrodes in P3HT:PCBM organic solar cells [27]. It was shown that the short-circuit current and efficiency of the solar cells were increased by a factor of ~2, whereas the open-circuit voltage was virtually unchanged by the addition of the nanotubes. Nevertheless, the power conversion efficiencies achieved so far are lower than 2%, which compares poorly with the performance of the same active layer P3HT:PCBM in a conventional ITO cell (around 5%, as reported by several laboratories [3]). Poor performance of CNT mesh in comparison to metal or ITO electrodes was also reported [28]. More recently, a spray patterned film of SWNTs (from aqueous solution using SDS as surfactant) was used as the electrode in a P3HT:PCBM solar cell and the efficiency was improved to 3.6%, which is comparable to conventional devices using ITO [29].

CNTs may be n-type or p-type doped in order to modify their semiconducting or metallic properties and improve the charge transport of a network (or entangled mat) of nanotubes [30, 31]. Raman characterization of doped nanotubes shows features in some bands that allow the amount of disorder to be quantified, in both nitrogen-doped [32] and boron-doped [33, 34] nanotubes. In this paper we report a detailed characterization of doped carbon nanotubes by atomic force microscopy (AFM), including scanning Kelvin probe microscopy (SKPM), and Raman spectroscopy. When 0.08 wt% concentration of CNTs, which is a small amount of nanotubes, is mixed with ZnO, it is shown that the work function of the mixture can be engineered according to the doping of the nanotubes. These electrodes give improved charge transport and additional flexibility for level matching in different kinds of organic optoelectronic devices, such as organic light emitting diodes and organic solar cells.

2. Sample preparation and experimental details

The samples were prepared following procedures described in detail in [35, 36]. They consist of thin films of three kinds: (i) ZnO, (ii) B-doped (p-type), N-doped (n-type) or undoped carbon nanotubes (CNTs) and (iii) ZnO blended with a small amount of doped or undoped CNTs, all of them deposited on fluor-doped tin oxide (FTO) substrates by spray pyrolysis in a glove box. All samples were stored in inert atmosphere at room temperature (glove box); they were only in contact with air during measurements. The CNTs had substitutional doping of electron-deficient boron (B) or electron-rich nitrogen (N), which systematically altered the work function of the CNTs: the doping levels of the B-CNTs and N-CNTs were 3.0 and 3.4 atom%, respectively [35]. The ZnO:CNT solutions were obtained from a precursor of zinc acetate dihydrate (Sigma-Aldrich, 16.5 mg) which was dissolved in 2-methoxyethanol (Sigma-Aldrich, 100 ml)
with stabilizer of ethanolamine (Sigma-Aldrich, 5 ml) and then mixed by ultrasonication for 4 h with 10.5 mg of the corresponding CNTs followed by centrifugation, precipitation and redispersion until a stable solution of the desired composition was obtained [36]. Finally, solution processing of thin films of ZnO/CNT (∼80 nm) nanocomposite layers and CNTs via spray pyrolysis on FTO (120 nm)/glass substrates was performed. The spray pyrolysis was carried on 400°C substrates using a hot plate and a conventional air-sprayer. The CNT content within the ZnO layer was maintained at 0.08 wt%. Previous UV–vis spectrum measurements have confirmed that the blended nanotubes do not significantly influence the bandgap (∼3.2 eV) or the optical transmittance of the ZnO layer [32].

All measurements were performed using an AFM manufactured by NT-MDT. The technique used was non-contact amplitude modulation AFM, in which tip oscillation is kept at a minimum to ensure a true non-contact regime. Topography and phase contrast images were acquired for scans of different sizes (ranging typically from 20 µm × 20 µm to 500 nm × 500 nm images).

All AFM tips were manufactured by NanoSensors (model: PPP-NCHPt50). They were conductive tips with a Pt–Ir coating (25 nm). The tips’ resonant frequencies were around 270 kHz and their force constants were around 40 N m⁻¹; the resonant frequency was determined for each tip used. Even if not necessary for AFM measurements, we used conducting tips because they were required for the SKPM measurements. This set of tips provided an X–Y plane resolution of Δx, Δy: ±25 nm and a height resolution of Δz ≤ 1 nm (tested against a calibration of a highly oriented pyrolytic graphite (HOPG) sample). The HOPG measurement also delivered a value of around 160 mV for the work function of the HOPG (4.6 eV), which provided a link to an absolute scale for the SKPM measurements, with a resolution (via Lorentzian fit) of ΔVcp: ±25 mV (see figures S-E1 to S-E3 in the supplementary information available at stacks.iop.org/Nano/24/484013/mmedia).

The SKPM measurements were performed using the second pass technique and applying an oscillating electrical field to the tip (sample grounded, second pass always at zero voltage). The lock-in technique was applied for the separation of harmonics, dc, 1ω, 2ω; the second feedback was used to nullify the first harmonic, and at this point the value of the applied Vdc = Vsurf was recorded (for a given X–Y position) and a surface potential image was constructed. The measurements were performed using a retrace mode in which the voltage applied to the sample piezo scanner was recorded in a first scan (with Vtip = 0), and this allowed us to perform a second scan at a given height on top of the recorded topography (the second scan did not use the first feedback; KPM was also performed without retrace mode, but in all cases we applied a second pass distance of 7 nm as explained above, working with the two feedbacks simultaneously).

Micro-Raman measurements were performed with a Renishaw In-Via spectrometer coupled to an optical microscope and using different excitation wavelengths: 785, 633, 514, 488 and 457 nm; the laser power was kept at 10 mW for all measurements (laser spot ∼1 µm²) unless indicated otherwise. Only excitation with 785 nm wavelength was performed at higher power: 80 mW. All spectra are presented as an accumulation of five acquisitions of 5 s each. Intensity is normalized to different peaks (as indicated in the respective figures).

3. Results and discussion

In this section, the experimental results and discussion are presented. First, we focus on the Raman spectra, both of pure CNTs and of blends of ZnO/CNTs; then the AFM and SKPM data are presented. Both sets of data enable the discussion of work function engineering and the demonstration that a tiny amount of CNTs can indeed modify the ZnO work function.

3.1. Raman spectroscopy

All Raman spectroscopy measurements show strong CNT signals for all the excitation wavelengths. This CNT signals are used to characterize the pure CNT samples and to demonstrate the combined signals of both ZnO and CNT when the spectra are measured on the blends, even for a tiny amount of CNT within the blend (0.08 wt%).

First, we analyse the CNT radial breathing modes [37, 38], which are related to the CNT diameter by

$$\omega_{\text{RBM}} = \frac{A}{d_0^2} + B$$

where $A = 227.0 ± 0.3 \text{ cm}^{-1}$ nm and $B = 0.3 ± 0.2 \text{ cm}^{-1}$. When the influence of the environment is strong, Van der Waals forces are included in the model [39],

$$\omega_{\text{RBM}} = \frac{227}{d_0^2} \sqrt{1 + C_d d_0^2}$$

with $C_d ≈ 0.05–0.07$.

Figure 1 illustrates the lower wavenumber spectra in which radial breathing modes (RBMs) are detected. It can be seen that both undoped and doped CNTs show RBMs, thus indicating that the substitutional incorporation of the doping atoms preserves the covalent structure of the nanotubes. The peak position does not show any dependence on the different excitation wavelengths, as can be observed in the intensities of the different CNT peaks: as expected for these first order peaks, neither the position nor the width of the peaks depends on the excitation wavelength. A detail of the peak at ~240 cm⁻¹ is shown for an excitation wavelength of 514 nm in figure 1. A peak at higher wavenumber (~310 cm⁻¹) is attributed to the signal from an inner nanotube (with
approximately half diameter). A summary of the diameters deduced from the measured RBM positions is presented in table S1 in the supplementary information (available at stacks.iop.org/Nano/24/484013/mmedia); the position of the peak and the full-width-half-maximum (FWHM) is obtained by fitting Lorentzian peaks to each individual measurement.

The G band, which corresponds to the tangential C–C stretching mode, can be easily identified and it is slightly modulated by the nanotube diameter, as indicated by

\[ \omega_G = 1591 - \frac{A}{d^2}, \]

where \( A \) can be \( A_{G+} = 0, A_{G-S} = 47.7 \text{ cm}^{-1} \text{ nm}^2 \) or \( A_{G-M} = 79.5 \text{ cm}^{-1} \text{ nm}^2 \); these values represent the small modulation of the main G peak (G+) for semiconducting (G-S) and metallic nanotubes (G-M), which creates a broadening of the G peak related to the orientation of the C–C stretching mode relative to the chirality of the nanotube [37, 41]. The D band (one phonon double resonance, DR1) is an LO or iTO mode, corresponding to an intervalley scattering (\( q = 2k \)). This D band is associated with disorder; it is a dispersive band and therefore \( \omega \) depends on the laser energy [40, 41], as can be seen in figure 4 (detailed values for the Raman shifts of the peak positions are included in table S2 in the supplementary information available at stacks.iop.org/Nano/24/484013/mmedia). The intensity ratio between the G and D bands allows us to define a parameter \( \delta = I_D/I_G \) calculated from normalized intensities which allows us to compare the degree of disorder between the undoped and doped nanotubes. The parameter \( \delta \) has been obtained for all excitation wavelengths (figure 3) and it shows that in the doped samples, the disorder is \( \sim 10\% \) larger than in the undoped sample; this arises from the random inclusion of substituting dopant atoms (N or B, 3–4%), but also from additional C–C disorder induced by the chemical doping process. Only for higher energy excitation does the undoped nanotube show a higher degree of disorder according to this definition. This higher degree of disorder is still not fully understood but it could be attributed to a more susceptible degradation of the undoped nanotube to the high energy laser.

The linear dependence of the Raman wavenumbers of the D and G’ peaks with excitation energy can be fitted with the following simple equation as shown in figure 4:

\[ \omega_{D,G'} = AE_{\text{laser}} + B. \]

The parameters \( A \) and \( B \) obtained from the fits are summarized in table 1. The dependence of the G’ peak is particularly interesting since it comes from a resonant second order, symmetry allowed, Raman scattering process involving an in-plane transverse optical (iTO) phonon, typical of all sp² carbon materials near the K point of the hexagonal Brillouin zone. A phonon with wavevector \(-2k\) will be selected by an electron with wavevector \( k \) in a double resonance process (if linear and angular momentum are conserved in the 1D carbon nanotube structure). If we consider that the energy of the laser is exciting electrons from the valence to the conduction band in the nanotube, \( E_{\text{laser}} = E_F - E_v = 2\hbar \nu k \), where \( v_F \) is the Fermi velocity of the electron, then the modulus of

![Figure 1](image-url)
Figure 2. Top: Raman spectra of doped and undoped CNTs for an excitation wavelength of $\lambda = 633$ nm normalized to the intensities of the G and $G'$ peaks respectively. The inset shows a detail of the G and $D'$ peaks. The shoulders at 1100 and 2500 cm$^{-1}$ are attributed to the FTO substrate. Middle: Raman spectra for B-doped CNTs (left) and N-doped CNTs (right) for four different excitation energies. The G peak is used for normalization. The strong intensity and Raman wavenumber variation of the D peaks can be appreciated. Bottom: Raman spectra for B-doped CNTs (left) and N-doped CNTs (right) for different excitation energies. The $G'$ peak is used for normalization. The strong intensity and Raman wavenumber variation of the $G'$ and 2LO peaks are easily appreciated, while 2G remains stable.

Table 1. Summary of the parameters obtained by fitting the plots shown in figure 4 to the linear equation which relates Raman shift wavenumber to the laser excitation energy.

<table>
<thead>
<tr>
<th></th>
<th>D band</th>
<th>G' band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$ (cm$^{-1}$ eV$^{-1}$)</td>
<td>$B$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>Undoped CNT</td>
<td>93 ± 13</td>
<td>1124 ± 29</td>
</tr>
<tr>
<td>B-doped CNT</td>
<td>40 ± 21</td>
<td>1246 ± 51</td>
</tr>
<tr>
<td>N-doped CNT</td>
<td>32 ± 62</td>
<td>1270 ± 15</td>
</tr>
</tbody>
</table>
Figure 3. The parameter defined to quantify disorder from the intensity ratio of peaks D and G ($\delta = I_D/I_G$) for undoped, B-doped and N-doped carbon nanotubes is plotted as a function of excitation energy.

the electron momentum $k$ can be changed by changing $E_{\text{laser}}$, and therefore Raman spectroscopy (phonon measurements) can be used to probe the electronic structure of the nanotube. According to the values shown in table 1, the doped nanotubes have a renormalization in electron and phonon energy when compared to the undoped ones: the $A$ parameter is reduced, indicating an increase in the electronic energy gap, while the $B$ (which is the $G'$ frequency at the $K$ point, where the dispersion relation of the iTO phonon has a minimum) is increased, indicating an upwards shift in the dispersion relation of the phonons in the more disordered (doped) nanotubes.

Finally, in figure 5 a Raman spectrum of the ZnO blended with undoped carbon nanotubes is presented in order to demonstrate that a simultaneous signal both from the ZnO and from the nanotubes can be achieved; it is shown for a Raman excitation wavelength of 633 nm. When the samples include a small amount of carbon nanotubes (0.08 wt%), the signal is dominated by the $G$, $D$ and $D'$ bands of the nanotubes which might be due to a stronger Raman scattering cross section of CNTs compared to ZnO; nevertheless, it is possible to get Raman spectra which simultaneously contain features from the ZnO, the FTO and the carbon nanotubes. (The features of pure FTO and ZnO/FTO samples are identified in the spectra shown in the supplementary information, sections C and F respectively available at stacks.iop.org/Nano/24/484013/mmedia.)

3.2. AFM measurements: topography and phase contrast

We took several images of topography and phase contrast, of different scan sizes, for all samples; two examples are shown in figures 6 and 7 for ZnO:N-doped and ZnO:undoped nanotubes. The analysis of the images focused on the extraction of the following parameters.

Figure 4. Peak positions for the D and $G'$ bands as a function of excitation energy for all kinds of nanotubes. Linear fits are superimposed on the plots and the resulting parameters are shown in table 1.

Figure 5. Raman spectrum of a ZnO + undoped CNT sample on an FTO substrate for $\lambda = 633$ nm excitation wavelength. The spectrum shows the simultaneous measurement of peaks attributed to FTO, to ZnO and to CNTs, all normalized to the G-CNT peak.
Figure 6. FTO/ZnO:N-doped CNT topography (left, $\Delta z = 45 \text{ nm}$), phase contrast (centre, $\Delta \phi = 8^\circ$) and contact potential (right, $\Delta V = 140 \text{ mV}$) images.

Figure 7. FTO/ZnO:undoped CNT topography (top left and right, $\Delta z = 35 \text{ nm}$) and contact potential (top centre, $\Delta V = 100 \text{ mV}$) images. The height profiles at the lines indicated in the images are shown in the bottom graphs.

(i) Peak-to-peak maximum height ($Z$): this is an automatic procedure which delivers a single number for each image and it has been applied to the larger scans. It allows us to detect anomalous protruding peaks. It is also a test for the relation of $Z$ and $X-Y$ resolution since the largest peak-to-peak maximum height value should not exceed the largest observed $X-Y$ feature for each sample and should be typically ten times the rms value of surface roughness; this is observed for all the samples.

(ii) Shape and size of the $X-Y$ features: manual measurement on the $X-Y$ plane of the image of the texture and grain’s aspect ratio for all the samples has been carried out. For the FTO substrate and unmodified ZnO, the shape of grains is rounded, but for the composite ZnO:CNT samples the shape is elongated and slightly larger. No clear correlation of the shape with the CNT doping is observed, with the exception of the ZnO:N-doped CNT sample for which systematically a small protruding tip always appears at one end of the elongated grain. This protruding tip creates a larger contrast in the phase images (see figure 6), indicating a different interaction between the protrusion and the rest of the sample. This different interaction could be provided by a segregation of one of the materials (improbable) or by the appearance of surface dipoles of the ZnO:CNT composite which change the tip–sample interaction for this particular location (these surface dipoles have been reported widely in the literature for pure ZnO samples [6]).

Finally, (iii) roughness (both average and rms) is automatically calculated for all scans, delivering a couple of values for each sample. For the rms calculations there is always a small dependence on the relative size of the scan and the $X-Y$ features of the sample, and therefore the values shown in table 2 are always taken for scans of $10 \mu\text{m} \times 10 \mu\text{m}$ for all samples to allow a better comparison between samples. All FTO/ZnO:CNT samples show a larger rms roughness compared to FTO, FTO/ZnO or FTO/CNT samples.

The AFM results are summarized in table 2. The analysis of the data shows that the grain size for ZnO is increased upon addition of nanotubes from around 150 nm (round shape) to larger grains of around $150 \text{ nm} \times 300 \text{ nm}$ (elongated shape). This result is remarkable given the small amount (0.08 wt%) of nanotubes present in the blend. Also, the roughness of
Figure 8. Surface contact potential histograms for (A) FTO/ZnO, (B) FTO/ZnO:undoped CNTs, (C) FTO/ZnO:B-doped CNTs and (D) FTO/ZnO:N-doped CNTs, and the corresponding Gaussian fits showing a bimodal distribution of contact potential values.

Table 2. Summary of AFM (topography and phase contrast measurements) of all samples. The values shown in the corresponding columns are averages of several measurements at different locations on the same sample for different samples of each kind.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max. peak-to-peak (nm) (±0.5 nm)</th>
<th>X–Y features (nm) (±25 nm)</th>
<th>Roughness average, rms (nm) (±0.5 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO</td>
<td>52.1 (±0.5 nm)</td>
<td>320–500</td>
<td>5.1, 6.6</td>
</tr>
<tr>
<td>FTO/ZnO</td>
<td>68.4 (±0.5 nm)</td>
<td>150–180</td>
<td>6.9, 8.7</td>
</tr>
<tr>
<td>FTO/ZnO:undoped CNTs</td>
<td>137.4 (±0.5 nm)</td>
<td>350 × 120 (elongated)</td>
<td>13.4, 16.8</td>
</tr>
<tr>
<td>FTO/ZnO:B-doped CNTs</td>
<td>139.4 (±0.5 nm)</td>
<td>300 × 150 (less elongated)</td>
<td>10.9, 13.9</td>
</tr>
<tr>
<td>FTO/ZnO:N-doped CNTs</td>
<td>186.1 (±0.5 nm)</td>
<td>350 × 230 (less elongated, protruding tips)</td>
<td>12.4, 16.0</td>
</tr>
<tr>
<td>FTO/undoped CNTs</td>
<td>72.9</td>
<td></td>
<td>7.7, 9.9</td>
</tr>
<tr>
<td>FTO/B-doped CNTs</td>
<td>73.9</td>
<td>Similar to FTO with some aggregations of carbon material</td>
<td>7.3, 9.7</td>
</tr>
<tr>
<td>FTO/N-doped CNTs</td>
<td>84.3</td>
<td></td>
<td>7.6, 9.6</td>
</tr>
</tbody>
</table>

the sample surface is increased upon addition of nanotubes (almost a twofold increase), and more protruding areas are sticking out of the surface.

3.3. SKPM measurements

For the SKPM measurements, a histogram of all images was systematically obtained; the statistical approach included several scans at different locations on the same sample (10), and also measurements of different samples of the same batch (4). The histogram of counts of the measured contact potential for each sample was then fitted using Gaussian peaks (see figure 8). In most of the samples, a single Gaussian peak was enough to get a good fit to the experimental data; a ‘noisy’ background (very broad Gaussian) was also included in some fits to account for intrinsic noise in our measurements. The experimental value, which measures contact potential differences within each image, can then be converted into an absolute work function value using the HOPG calibration performed for all tips (see details in the supplementary information available at stacks.iop.org/Nano/24/484013/mmedia). For each sample, both the measured surface contact potential and the calculated work function are presented in table 3. For some of the images, the appearance of a bimodal distribution of values was evident by eye, but the histogram showed it without doubt via the use of two Gaussian peaks of similar width to fit the experimental histogram. This is the clearly the case for the two composite samples which combine ZnO and doped CNTs; for the ZnO:undoped CNT sample two Gaussians are also needed although both are
Figure 9. FTO/undoped CNT topographic (left, Δz = 100 nm) and surface contact potential (KPM, centre, ΔV = 250 mV) images. The histograms of surface contact potential measurements and the corresponding Gaussian fits are shown for all the CNT samples: FTO/undoped CNTs, FTO/B-doped CNTs and FTO/N-doped CNTs.

Table 3. Summary of the SKPM results on all samples. The measured surface contact potential and the obtained work function after calibration are shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured contact potential (mV) (±25 mV)</th>
<th>Work function (using HOPG calibration) (eV) (±0.1 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO</td>
<td>360</td>
<td>5.0</td>
</tr>
<tr>
<td>FTO/ZnO</td>
<td>−270</td>
<td>4.3</td>
</tr>
<tr>
<td>FTO/ZnO:undoped CNT</td>
<td>0</td>
<td>4.6</td>
</tr>
<tr>
<td>FTO/ZnO:B-doped CNT</td>
<td>220, 300</td>
<td>4.9</td>
</tr>
<tr>
<td>FTO/ZnO:N-doped CNT</td>
<td>−205, −225</td>
<td>4.4</td>
</tr>
<tr>
<td>FTO/undoped CNT</td>
<td>10</td>
<td>4.6&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>FTO/B-doped CNT</td>
<td>370</td>
<td>5.1&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>FTO/N-doped CNT</td>
<td>−320</td>
<td>4.3&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Results for pure nanotubes on FTO; the statistical procedure for obtaining the work function is different from that for the rest of samples as explained in the main text.

centred at the same V<sub>cp</sub> value (without the second Gaussian it is not possible to fit the height of the ‘apparently’ single peak, see figure 8(B)). For the samples of only CNTs on FTO, the appearance of the SKPM is different. It seems that aggregations of carbonaceous material provide a non-uniform value of the contact potential. The CNTs are not seen in the topographic images, although if a histogram of only the ‘aggregation’ areas is taken in the contact potential images (the number of counts is much lower compared with the previous histograms), the Gaussian fit provides values that allow us to distinguish the different dopings of the CNTs (see figure 9, and values in table 3 marked with an ‘a’). The work function has been obtained for these pure nanotube on FTO samples following the same procedure as explained above; the values obtained are (i) 4.6 ± 0.1 eV for FTO:undoped CNTs; (ii) 5.1 ± 0.1 eV for FTO:B-doped CNTs; and (iii) 4.3 ± 0.1 eV for FTO:N-doped CNTs. All these values, obtained from the SKPM measurements, are very similar to the values obtained by ultraviolet photelectron spectroscopy (UPS) [36] and electron energy loss spectroscopy (EELS) [35] measurements for the same material.

The most important result is the demonstration that the work function of the pure nanotubes can be transferred to the ZnO:CNT blend even if the amount of nanotubes is small (0.08 wt%), delivering values for the work function of 4.6 ± 0.1, 4.9 ± 0.1 and 4.4 ± 0.1 eV respectively. The CNT is acting as a doping agent for the ZnO without the need for structural modification of the wurtzite structure of ZnO; furthermore, the ZnO:CNT samples are very uniform and variations of the measured parameter between different samples are within the error margin of the measurements (±25 mV). This is not the case for the pure CNT samples (doped or undoped), where although the samples are globally similar to each other, there is a higher variation of the value of the measured contact potential within the same sample, as can be seen in figure 9, where the data dispersion is larger, both for the value of the contact potential (around ±40 mV, almost twice the experimental error for the measurement, which is ±25 mV) and for the number of counts for each value. Interestingly, the dispersion between different locations on the sample disappears for the ZnO:CNT samples, indicating that the small amount of CNTs is uniformly dispersed and modifies the value of the contact potential of the whole surface without variations from one spot to the next (at least for the 10 spots that were measured within each sample).

The experimental results demonstrate that control of the work function of ZnO:CNT blends has been achieved. This can be exploited in the design and fabrication of both organic solar cells (OSC) and light emitting diodes (OLEDs), where an optimum match between the electrodes and the HOMO or LUMO levels of active materials is required for a good performance of the device. This is usually achieved by the inclusion of different interfacial charge transport layers that can be considered as electron (or hole) blocking...
layers. In particular, for the case of OSCs, the fabrication of inverted structures (ITO acting as cathode) which have similar efficiencies but are more stable than the equivalent standard structure (ITO acting as anode) requires the inclusion of a ZnO layer, which works well for the P3HT:PCBM active layer, but which will require a slightly different value for the work function if a polymer with lower band gap (and different HOMO level) is used in the solar cell: this new required value can be achieved upon addition of the corresponding doped CNTs to the ZnO-based interlayer. Similarly, for OLEDs, polyelectrolyte polymers have been used as hole injecting layers with good results; ZnO:CNT interlayers can similarly be used to modify the work function but without the additional complication of built-in charges that appear in the case of polyelectrolytes. Nevertheless, some processing issues need to be addressed in order to obtain a successful device with the new ZnO:CNT interlayer: first, the high temperature of the substrates during the pyrolysis process involved in the sample preparation should be reduced if flexible plastic-based substrates in an R2R processing line are going to be used; secondly, the carbon nanotubes may occasionally protrude from the surface, as shown in table 2 for the maximum peak-to-peak height, which considerably exceeds the rms value of surface roughness; these protrusions may create shorts and therefore reduce the performance of the devices (lower the shunt resistance of even completely shunted devices).

4. Conclusions

Doped and undoped carbon nanotubes (CNTs) have been characterized by Raman spectroscopy using different wavelength excitations. The Raman spectra demonstrate that the CNTs keep their covalent structure after being substitutionally doped by 3–4% of nitrogen or boron atoms, delivering respectively n-type and p-type semiconducting material. Raman spectroscopy allowed us to characterize the CNTs kept their covalent structure after being substitutionally doped by 3–4% of nitrogen or boron atoms, delivering respectively n-type and p-type semiconducting material. Raman spectroscopy allowed us to characterize the CNTs and substitutionally doped by 3–4% of nitrogen or boron atoms, delivering respectively n-type and p-type semiconducting material. Raman spectroscopy allowed us to characterize the CNTs and substitutionally doped by 3–4% of nitrogen or boron atoms, delivering respectively n-type and p-type semiconducting material. Raman spectroscopy allowed us to characterize the CNTs. Doping of the CNTs surface with nitrogen or boron results in a change of their electronic properties, which can be used to tune the work function of the surface.

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Appendix. Work function measurements by scanning Kelvin probe microscopy

Reliable measurements of the work function with submicron resolution in air can be achieved by means of scanning Kelvin probe microscopy (SKPM). Two general modes for AFM measurement can be used. The first is a mechanically driven mode in which a voltage $V_{\text{piezo}}$ is applied to the small piezo of the cantilever while the tip is kept at ground or fixed bias ($V_{\text{tip}} = 0$ or $V_{\text{tip}} = V_{\text{dc}}$ constant),

$$V_{\text{piezo}} = V_{\text{dc}} + V_{\text{ac}} \sin (\omega p t)$$

where $z$ is the tip–sample distance. Then, the detection of resonant frequency shift is performed while feedback adjusts $\omega p$ (the ‘driving’ frequency) in order to keep maximal $A(\omega p)$ (frequency dependent oscillation amplitude). An alternative is detection of amplitude change or phase shift, both at constant $\omega p$, which is the mode that we used in the AFM used for our topography and phase measurements.

The second mode can be called the voltage modulation mode, in which the driving voltage of the piezo is set to zero ($V_{\text{piezo}} = 0$) and a conductive tip is biased by a dc $+ \text{ac}$ voltage given by

$$V_{\text{tip}} = V_{\text{dc}} + V_{\text{ac}} \sin (\omega t)$$

where $z_0$ is the tip–sample separation when $V_{\text{tip}} = 0$ and $A_0$ is the static response, and two sets of amplitude and phase response (first and second harmonic) can be separated by lock-in techniques and used for Kelvin probe microscopy techniques.

When there exists electrostatic interaction, the force is described by

$$F_{el} = \frac{1}{2} (\Delta V)^2 \frac{\partial C(z)}{\partial z} + \frac{Q_i Q_t}{4 \pi \varepsilon_0 z^2}$$

where $\Delta V$ is the difference in potential between the sample and the tip, $V_{\text{tip}} - V_{\text{surf}}$, $C(z)$ is the tip–sample capacitance and $Q_i, Q_t$ are the electrostatic charges of the sample and the tip. If there is no surface charge or built-in surface dipoles, the second term of the right hand side is much smaller than the first one and it is a good approximation in Kelvin probe microscopy.
microscopy (KPM) to consider only the capacitance variation with tip–sample distance. In this case, substituting
\[ \Delta V = V_{\text{tip}} - V_{\text{surf}} \]
and considering \( V_{\text{tip}} \) as a superposition of dc and ac voltages as described in the equation above, we obtain
\[
F(z) = \frac{1}{2} \frac{\partial C(z)}{\partial z} \left[ (V_{\text{dc}} - V_{\text{surf}})^2 + \frac{1}{2} V_{\text{ac}}^2 [1 - \cos (2\omega t)] \right]
+ 2 (V_{\text{dc}} - V_{\text{surf}}) V_{\text{ac}} \sin (\omega t)
\]
which can be separated into three terms
\[ F = F_{\text{dc}} + F_{\text{1ao}} + F_{\text{2ao}} \]
which are, respectively,
\[
F_{\text{dc}}(z) = \frac{1}{2} \frac{\partial C(z)}{\partial z} \left[ (V_{\text{dc}} - V_{\text{surf}})^2 + \frac{1}{2} V_{\text{ac}}^2 \right]
F_{\text{1ao}}(z) = \frac{\partial C(z)}{\partial z} (V_{\text{dc}} - V_{\text{surf}}) V_{\text{ac}} \sin (\omega t)
F_{\text{2ao}}(z) = -\frac{1}{4} \frac{\partial C(z)}{\partial z} V_{\text{ac}}^2 \cos (2\omega t).
\]
Lock-in techniques enable us to extract \( F_{\text{1ao}} \), then a feedback loop to \( V_{\text{dc}}(\text{tip}) \) is employed to keep it equal to zero, so \( F_{\text{1ao}} = 0 \) and then \( V_{\text{dc}} = V_{\text{surf}} \), therefore mapping the surface potential (Kelvin probe microscopy). The second harmonic signal provides information about the \( z \)-derivative of the capacitance. The information achieved by this technique can deliver directly the differences in surface potential between different parts of the same sample (ideally within the same image); this information can be obtained by statistical treatment of the pixelated image. In order to provide absolute values of the work function of the measured surface, it is necessary to calibrate the tip using a well known sample, usually a fresh surface of highly oriented pyrolytic graphite (HOPG), and then convert the relative surface potential measurements to absolute work function values. Ideally the tips should be calibrated before and after each experiment.

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