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The effect of adsorbed species and exposure to sulfuric acid on the electrical conductance of individual single-wall carbon nanotube transistors

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The electrical conductance of individual single-wall carbon nanotube (SWCNT) transistors was investigated before, during, and after soaking in concentrated sulfuric acid in air environment. The resulting doping effect has induced a shift of the Fermi level which was monitored by the electrical behavior and sought in Raman spectroscopy signature. For either metallic or semiconducting SWCNTs, the maximum conductance value was lowered during the contact with the acid; remained low for a short time after removing the acid; and recovered after long air exposure. This demonstrated the significant contribution of the physisorbed species in the measurements, specifically at the metal pad/SWCNT contact lines. The study also demonstrated that washing with sulfuric acid is an easy method for removing adsorbed species and reaching the intrinsic conductance of SWCNT-based devices.

Single-wall carbon nanotubes (SWCNTs), whose regular diameters are in the 1–2 nm range, have attracted a lot of attention as promising nanosized components for applications in nano-scale devices, specifically regarding their transport properties. Modifying SWCNT properties through pressure, doping and adsorption of species has become a domain of growing interest, from both experimental and theoretical points of view [1,2]. In this regard, the conductance of SWCNT mats was found to increase with oxygen partial pressure [3], mainly due to tunneling between SWCNTs assisted by physisorbed molecules [4]. The conductance of individual metallic SWCNTs was found to switch from ballistic to diffusive as the distance between the electrodes increases. Within the ballistic regime, the conductance could be modified by moving the Fermi level, which changes the number of quantum channels available. For devices, properties were modified through electrostatic gating, change in gate coupling, carrier mobility, and Schottky barrier effects [5]. Chemical doping is however an alternative route to consider.

Chemical doping of SWCNT-based devices by liquids was studied for SWCNT mats [6,7], and soaking in either nitric or sulfuric acid was found to increase dramatically the

conductance of the mat [6]. On the other hand, nitric acid or a mixture of nitric and sulfuric acids can modify the SWCNT structure after a while (as evidenced by the occurrence of a D band in Raman spectra), while sulfuric acid leaves the SWCNT unaffected [6]. From a theoretical point of view, sulfuric acid is interesting to study as protonation and charge transfer were revealed experimentally [6] while not fully confirmed by calculation [8], certainly because effects induced by defects and the dissociation of species were not considered. In order to give more insights on the mechanisms involved in the acid treatment of SWCNT-based nanodevices, we report here a detailed investigation of the Raman spectroscopy and electrical properties of individual semi-conducting (s-) and metallic (m-) SWCNTs before, during, and after soaking in sulfuric acid. We show the influence of the acid on the intrinsic properties of the SWCNTs and on the electrical contact with metal electrodes. Interestingly, the procedure was revealed an easy, mild, and flexible alternative (with respect to, *e.g.*, UV irradiation or heat-treatment) for cleaning SWCNT-based devices and accessing their intrinsic behavior, which makes it a valuable facility for the lab-on-chip technology.

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SWCNT-based transistor-type devices (Fig. 1a) were built using a degenerately n-doped silicon substrate topped with a 300-nm-thick thermally-grown SiO_2 layer as a back-gate. CCVD-prepared SWCNTs were bought from TIMESNANO. The SWCNT deposition procedure is described elsewhere [9]. The nanotubes lying on the substrate were rinsed with deionized water (for removing the surfactant) then checked to be individual using atomic force microscope (AFM), subsequently confirmed from the Raman spectrum intensity and shape, and the conductance measurements. Some SWCNTs were then contacted with 80 nm-thick Pd electrodes by aligned e-beam lithography. The selected SWCNTs had a typical diameter of 1.4 nm. The length between the source and drain electrodes was $1.4 \mu\text{m}$ for the s-SWCNT and $0.7 \mu\text{m}$ for the m-SWCNT investigated in Figs. 2 and 3. *In situ* chemical doping with sulfuric acid (18 M) of the contacted SWCNTs was then carried out by the μ -pipette deposition technique (Fig. 1b). This was Step 2, considering that Step 1 corresponds to the as-prepared starting devices. The acid droplet size could be controlled as small as a few microns as shown in Fig. 1c. It is worth noting that, with larger droplets, no Raman signal could be recorded because adding a droplet with a high refractive index (1.7) reduces the light onto the nanotube and dramatically modifies the laser spot shape. It was therefore a key condition to deposit droplets as small as possible. Dedoping was achieved by washing the droplet out with distilled water and then drying the devices under nitrogen flow (Step 3). The devices were then left for 24 h in open air (Step 4).

Room-temperature Raman spectra were obtained using a XploRA™ spectrometer (with automatic switching facility allowing the alignment to be kept while changing the exciting wavelengths) in backscattering configuration using a $\times 50$ objective with a low laser output power to avoid heating effect (1.5 mW at 532 nm and 3.0 mW at 638 nm). Fig. 2a shows the G band region of the Raman spectrum of an individual s-SWCNT after Step 2 (doped, top panel) and then after Step 3 (freshly dedoped, bottom panel) using the 2.33 eV laser excitation energy (no signal at 1.94 eV). Fig. 2b shows the same for a m-SWCNT using the 1.94 eV laser excitation energy (no signal at 2.33 eV). The G band for SWCNTs is composed of a G^+ mode near 1593 cm^{-1} and a G^- mode which is diameter dependent. The G^- mode is typically a large Fano shape [10] for the m-SWCNTs excited with red wavelength (E_{11}^m energy transition). A simple Lorentzian fits the G^- mode better for s-SWCNTs excited with the green wavelength (E_{33}^{SC} energy transition). The consequence of sulfuric acid doping on the Raman spectra (Fig. 2) is complex. The integrated intensity is reduced [6] as the Fermi level moves in the valence band, and the Fano shape of the G^- mode is reduced as well [6]. Electron-phonon coupling modifies the position of the G peak. In our spectra, no large shift was observed. For the m-SWCNT, the Fano coupling was reduced and for the s-SWCNT, the intensity was reduced as expected when p-doping is considered.

Electronic properties were monitored from Steps 1 to 4 at room temperature and open air (Fig. 3). The drain electrode was grounded in all of the measurements and the gate voltage was swept from -9 to 9 V. Before acid-doping (Step 1), the conductance versus back-gate-voltage ($G = f(V_g)$) for s-SWCNT devices exhibited a typical semiconducting behavior (black plot in Fig. 3a). The reported hysteresis is often observed with

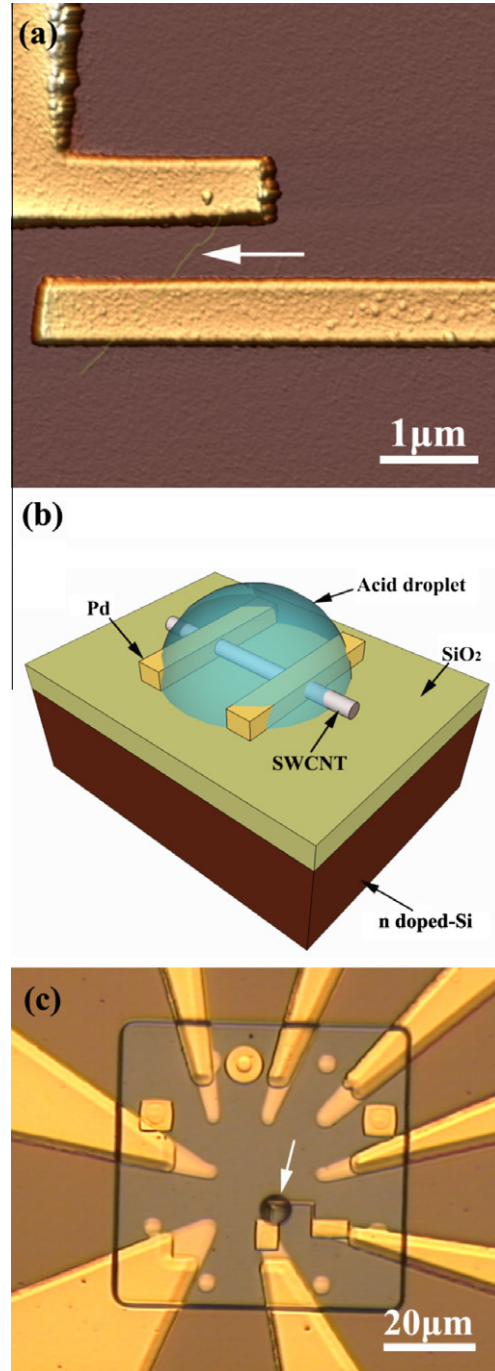


Fig. 1 – (a) Typical AFM image of an individual-SWCNT-based device. The arrow indicates the location of the SWCNT contacted by two Pd electrodes. (b) Sketch of a device at Step 2 (i.e., after *in situ* deposition of a sulfuric acid micro-droplet on the device). (c) Optical image showing the chip and the acid micro-droplet (arrow).

s-SWCNT transistor [11]. As expected, once being put in contact with the droplet of sulfuric acid (Step 2), a switch from the semiconducting behavior to a metallic behavior was observed (red plot in Fig. 3a), yet accompanied by a drop of the maximum conductance value. Right after removing the acid by rinsing the device with water (Step 3), the semiconducting behavior was restored, yet without affecting the maximum

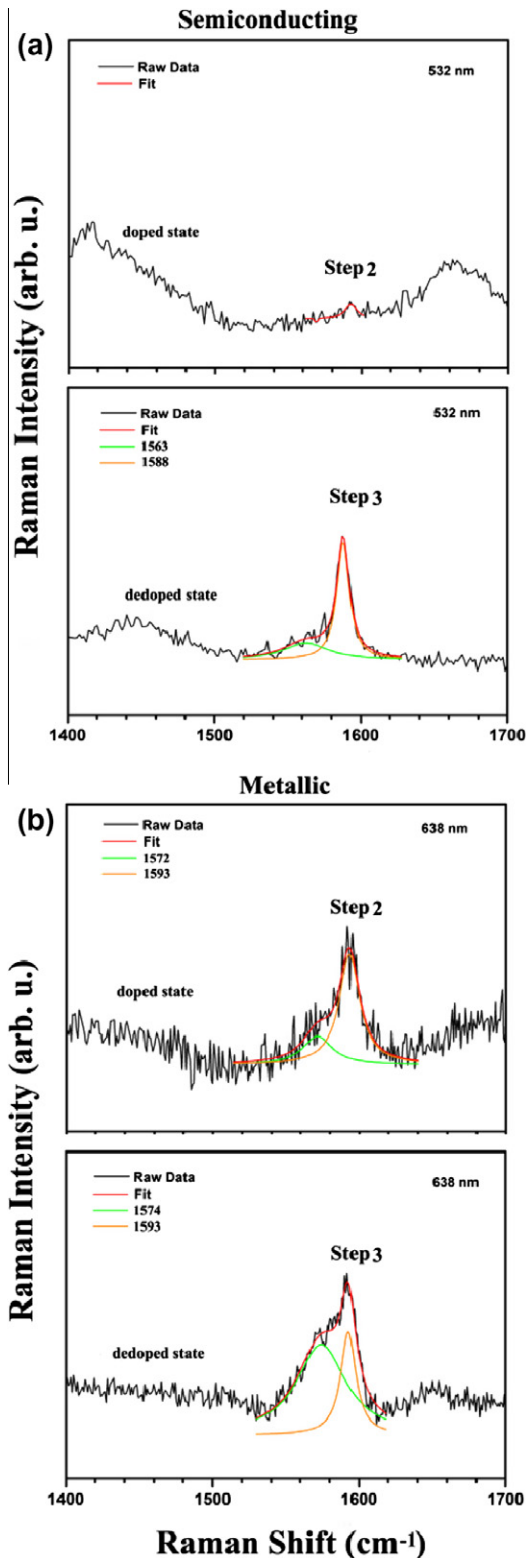


Fig. 2 – Raman spectra of acid-doped (Step 2, top panels in (a) and (b)) then dedoped (Step 3, bottom panels in (a) and (b)) SWCNT devices in the G-band region. (a) Spectra for a semiconducting SWCNT device with green (532 nm) probe. (b) Spectra for a metallic SWCNT device with red (638 nm) probe. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

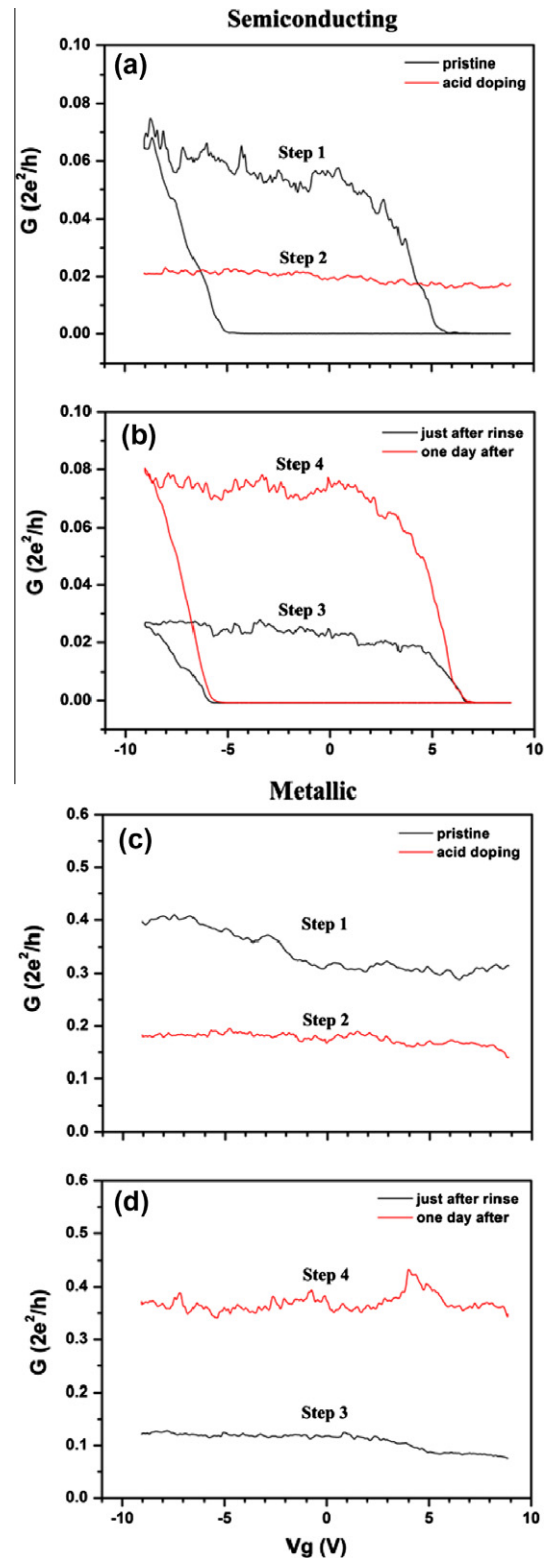


Fig. 3 – (a) Characteristics of a s-SWCNT field-effect transistor before (black plot, Step 1) then after sulfuric acid doping (red plot, Step 2). (b) Transport behaviors of the same semiconducting SWCNT right after dedoping (black plot, Step 3) and after 24 h of exposure to air (red plot, Step 4). (c) and (d) are the same, with a m-SWCNT. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

value of the conductance, which remained low. The doping of s-SWCNT by sulfuric acid is therefore a reversible process which allows a control of the electronic properties of the device to be achieved. Interestingly, the initial high conductance observed for the starting s-SWCNT (Step 1) was recovered after several hours of air exposure (Step 4) as shown in Fig. 3b.

Fig. 3c shows the $G = f(Vg)$ plot of a m-SWCNT device. An apparent metallic transport behavior was always observed. Measuring the conductance of the m-SWCNT while in contact with the sulfuric acid droplet (Step 2, red plot in Fig. 3c) induced again a decrease with respect to Step 1. Removing the acid (Step 3) did not affect the conductance value, which again remained low. The initial conductance of the m-SWCNT devices was also recovered after several hours of air exposure (Step 4, Fig. 3d). In a separate experiment where a sulfuric acid droplet was deposited across the gap between two Pd pads free of any SWCNT, it was checked that the acid did not show any conductance by itself.

The decrease in conductance upon the contact with sulfuric acid, and the long time recovery of the initial conductance were observed with all samples. This effect therefore does not originate from any intrinsic property of the SWCNTs but from other features such as the SWCNT/electrode contact and/or the presence of adsorbed species. H_2SO_4 is a strong dopant and O_2 a weak one. Hence, comparing Step 2 (doped), Step 3 (dedoped, rinsed, and dried), and Step 4 (dedoped, rinsed, dried, and air exposed) leads to the only possible conclusion that the mechanism involved relates to a Schottky barrier effect between the SWCNT and the Pd pads [5]. Indeed, O_2 can enhance the transmission of electrons at the SWCNT/Pd contact line by letting them hop via the molecular orbitals, as already observed between SWCNTs in mats [4]. When putting the SWCNTs in contact with sulfuric acid, the protonating H^+ ions are able to p-dope the s-SWCNTs but meanwhile also react with the physisorbed O_2 and remove them from the adsorption sites [12]. As no doping effect remained right after rinsing, it is assumed that the SWCNT surface and Pd/SWCNT contact lines are merely cleaned with no charges nor adsorbed species left. Moreover, since the semiconducting-to-metallic behavior switching upon doping was found to be fully reversible upon dedoping, it is demonstrated that concentrated sulfuric acid clearly does not affect the quality of contact between the Pd electrodes and the s- or m-SWCNTs. The apparent contradiction with what was observed in literature for SWCNT mats, i.e., an increase of the conductance upon soaking in H_2SO_4 [6], instead of a decrease is likely to come from the fact that mats contain both m- and s-SWCNTs, and that doping all the s-SWCNTs in the mats result in dramatically increasing the number of conduction channels [6], in an extent that overcome the drop in conductance resulting from cleaning the SWCNT surface and contact area from the physisorbed species. This collective behavior cannot be observed for individual SWCNTs.

To summarize, single micron-size droplets of concentrated sulfuric acid were able to be deposited onto single-SWCNT-based transistors. The resulting doping effect on the SWCNTs was then able to be studied *in situ*. As expected, sulfuric acid, as a strong dopant, is able to switch the behavior of a single semiconducting SWCNT to metallic. On the other hand, as opposed to what happens with SWCNT mats, sulfuric acid is shown to decrease the apparent conductance for both s-

and m-SWCNTs. This is explained by considering the Schottky barrier at the metal electrode/SWCNT contact lines, which is modified by the physisorption of species from air, then by the subsequent removal of the latter. From a practical point of view, we confirm for individual SWCNTs earlier statements established for SWCNT networks, that is to say, the electronic behavior (*e.g.*, the conductance values) of SWCNT-based devices reported in the literature should be taken with caution if not carried-out in inert (Ar) or vacuumed atmosphere. Alternatively, we also demonstrate that sulfuric acid, which is a strong acid and moderate redox liquid, is able to suitably clean SWCNT-based devices without significantly affecting anything else of such devices. Sulfuric acid soaking hence appears as a cheap, fast, mild, and easily operable procedure for cleaning electronic devices whose intrinsic behavior is of interest, making it a specifically useful tool for nanoelectronics-related (*e.g.*, lab-on-chip devices) technology.

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