Gas sensing improvement of carbon nanotubes by NH$_4$OH–flash treatment: a nondestructive purification technique†

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Surface carbonaceous impurities are removed from carbon nanotubes by NH$_4$OH–flash treatment and microscopic analyses reveal that the carbon walls retain integrity and the tube resistance is reduced by 17% of the initial value. Clean tubes exhibit a significant improvement on gas sensitivity and O$_2$ adsorption–desorption becomes reversible.

Single-walled carbon nanotubes (SWCNTs) made by arc discharge or pyrolysis are usually accompanied by carbonaceous materials appearing as tube surface impurities. The conventional technique employs radical oxidation for nanotube purification and tube wall damage is inevitable. Physical approaches such as filtration and centrifugation of SWCNT dispersed solutions are inefficient and sample purity reaches 80% at most. In this work, NH$_4$OH–flash treatment is found capable of removing tube surface impurities and clean tubes exhibit (i) lower resistance, (ii) reversible O$_2$ adsorption–desorption, and (iii) faster gas sensing performance, compared with pristine samples. A novel SWNT purification mechanism is proposed and verified.

SWCNTs were synthesized according to a reported method and the as-made materials (100 mg) were immersed into NH$_4$OH (Showa, 28 vol%), followed by ultrasonic agitation for 10 minutes. A thin SWNT film extracted from the solution was suspended between silver electrodes pre-defined on a glass substrate and the device was then placed in a stainless steel chamber filled with N$_2$ (1 atm). The film was consecutively flash heated (3–5 times, 50 mW, Fig. 1a).

Fig. 1b shows a purified SWCNT film from the current method and the bundle diameter appears to be smaller than that of the pristine samples by ca. 10%; the morphology of SWCNTs before and after NH$_4$OH–flash treatment is shown in the electronic supplementary information (ESI,† Fig. S1). Raman spectra and thermo-gravimetry (TGA) also support the purification effect from our technique; particularly, tube integrity is preserved after the process (ESI,† Fig. S2). In addition to carbonaceous materials the catalytic particles also vanish and Fe content is reduced to 0.1 at% (ESI,† Table S1). This is novel because elimination of Fe encapsulated particles by conventional acid treatment usually leads to tube-wall functionalization and dissociation of sp$^2$ species. In our electron microscope study, traces of defective carbon cages were frequently detected at criss-crossed tubes (arrows, Fig. 2a,b) and their dimensions are similar to those of catalytic particles seen in raw materials.† We find that the soaking of SWCNTs in aqueous ammonia is a key procedure and surface impurities cannot be directly eliminated by flashes prior to NH$_4$OH treatment. This is verified by the following experiments. A pristine film was partially immersed into NH$_4$OH solution and Fig. 3a shows wetted (A) and unwetted (B) regions at low magnification. The enhanced image exhibits that the wetted area is partially covered with thick carbonaceous materials which aggregate possibly during solution treatment (Fig. 3b). The film was then flashed and Fig. 3c,d displays the wetted and unwetted regions respectively after flashes; the former is purified while the latter remains unpurified. According to the above observations we propose a novel purification mechanism for the current study. When pristine SWCNTs are treated with concentrated NH$_4$OH the surface carbonaceous materials absorb large amounts of solution. The flash then triggers exothermal oxidation (Fe + O$_2$ → Fe$_3$O$_4$ or Fe$_2$O$_3$) and the released heat decomposes NH$_3$ into N$_2$ and H$_2$. Ammonia ignition subsequently occurs via the reverse Haber–Bosch process and the explosion blasts the impurities away.

$\text{N}_2(g) + 3\text{H}_2(g) \xrightarrow{\text{Fe}_2\text{O}_3 \text{ or Fe}_3\text{O}_4} 2\text{NH}_3(g)$ \hspace{1cm} $\Delta H^\circ = -92.0$ kJ

The following evidence supports our explosion theory. First, the heat released from oxide formation reaches 1500 °C, sufficient for the reverse process. Second, according to a Langmuir plot of adsorbed ammonia on SWCNTs, a monolayer of NH$_3$ with 26% coverage on the nanotube surfaces yields a similar NH$_3$.
concentration at elevated temperature, and a monolayer of NH$_3$ is equivalent to equilibrium coverage of 0.26.11–13 In our experiment, SWCNTs were treated with 28 vol% NH$_4$OH (14.28 M) at ambient pressure and equilibrium ammonia coverage on the tube surfaces should reach a flammable condition (15–28%), meanwhile, surface impurities are high surface area materials (1315 m$^2$ g$^{-1}$)14 therefore ammonia gas trapped in surface impurities must be greater than 15%. Third, carbon debris produced by explosion has been observed in the trench region below the suspended film (Fig. 1a). SEM-EDX analyses show that the debris consists of carbonaceous and oxide particles, along with shorter SWCNTs (Fig. 1c,d). Fourth, rapid removal of surface impurities by chemical blasts should result in a resistance drop rather than a curve, which is evident by Fig. 4a. The profile shows stepwise structures and each step represents a resistance drop caused by a single flash. At the 4th flash, the nanotube film becomes purified (Fig. 1b) and resistance is reduced by 17% of the initial value. It is noteworthy that the contribution of surface scattering to nanotube resistance has not been previously characterized and the value obtained here is based on the sum of $R/R_0$ reduction at each flash, i.e. 7% + 7% + 2% + 1% = 17% (insert, Fig. 4a). Fifth, the photoacoustic effect associated with the blast has been detected (Fig. 4b) and the sound intensities for flashing on the glass substrate, pristine and NH$_4$OH treated SWCNT films (b), and H$_2$ generation by consecutive flashes for background, pristine and NH$_4$OH treated SWCNT films; the background and pristine film curves overlap (c).

Fig. 2 Enhanced SEM image of flash-treated SWCNTs; arrows denote the residual particles at criss-crossed tubes (a), TEM images of flash-treated SWCNTs; arrows denote the residual particles clamped by criss-crossed tubes (left, b) and enhanced TEM images verify that particles are defective carbon cages (right, b).

Fig. 3 NH$_4$OH wetted (denoted as A), and unwetted regions (denoted as B) (a), enhanced SEM image of both regions (b), region A after flashes (c) and region B after flashes (d).

Fig. 4 Variation of SWCNT resistance with consecutive flashes (a); insert shows the magnitude of resistance reduction at each flash. Photoacoustic response of background, pristine and NH$_4$OH treated SWCNT films (b), and H$_2$ generation by consecutive flashes for background, pristine and NH$_4$OH treated SWCNT films; the background and pristine film curves overlap (c).
powers respectively; namely, the effect recorded from the NH4OH treated sample is 2.5 dB = (69.2 – 66.7) = 28% greater than the untreated film. Sixth, the H2 gas content increases significantly between 1–4 flashes (13 ppm, Fig. 4c), indicative of NH3 explosion (decomposition); no H2 was produced by flashing the untreated sample. Seventh, particles held by criss-crossed tubes survive the blast (arrows, Fig. 2a,b) while other attached impurities vanish.

The current technique was applied to a thick SWCNT deposit (2 mm) on s glass substrate and the purifying effect was found to be inefficient. This is due to flash shielding by surface nanotubes so interior SWCNTs remain unaffected. Our method however appears to be useful for devices made from thin films or individual SWCNTs, for example, the O2 sensitivity of a SWCNT film can be significantly improved by an ammonia blast. Fig. 5a shows that trapped air has further evolved into chemisorbed O2 (decomposition); no H2 was produced by flashing the untreated sample. From the tubes. Secondly, R/Re of the pristine SWCNT film increases relatively slowly during chamber evacuation (760 → 10^-4 Torr) compared with the purified nanotubes, revealing air trapping by impurities. Trapped air means that O2 is still interacting with tubes (charge transfer) which accounts for R/Re fluctuation (dark curve between vertical lines, Fig. 5a). Similar fluctuation is absent in the purified nanotubes under the same regime, implying complete O2 desorption from the tubes. Secondly, R/Re saturation at different values suggests that trapped air has further evolved into chemisorbed O2 (i.e. R/Re at 1.009 and 1.032 for pristine and purified samples). At the chamber ventilation stage, clean tubes allow direct O2 adsorption so R/Re decreases rapidly. In contrast, hindrance of gas adsorption by surface impurities leads to slow resistance reduction, meanwhile, a small feature present in Fig. 5a (circle) is due to the following: (i) when gas is introduced into the chamber the surface impurities are slightly compressed, thus promoting surface scattering and resistance; (ii) molecules then diffuse into carbonaceous coverage to establish the O2-tube interaction and resistance decreases accordingly. Again, R/Re of pristine SWCNTs does not return to the initial value at 760 Torr, attributable to chemisorbed O2 (Fig. 5a). Based on Fig. 5a, we conclude that O2 absorption–desorption is irreversible and reversible on pristine and purified SWCNTs respectively. We now compare the gas detection performance before and after chemical explosion, and the O2 sensitivity of SWCNTs is estimated by eqn (1)^15

\[
\phi = k_B T \ln(R/Re) + \Delta \phi
\]

where \(\Delta \phi\), \(R\) and \(\Delta \phi\) are the SWCNT work function, resistance and electron affinity, respectively. The electron affinity is defined as the gap between the vacuum level and the lowest edge of the conduction band, so \(\Delta \phi\) is not affected by charge transfer (O2 adsorption) and eqn (1) can be simplified as

\[
\Delta \phi = k_B T \ln(R/Re)
\]

Substitution of \(T = 300\) K, \(k_B\) (Boltzmann constant) and equilibrium \(R/Re\) ratios (1.031 for purified and 1.009 for pristine) into eqn (2) gives \(\Delta \phi = 0.25\) meV for pristine and \(\Delta \phi = 0.78\) meV for purified samples respectively; the larger the \(\Delta \phi\) the greater the O2 doping concentration. Fig. 5a is then fitted by an exponential decay function as given in eqn (3):

\[
[N/N_o + 1] \propto R/Re = 1 + C \exp(-\lambda t)
\]

where \(N\) and \(N_o\) are O2 coverage at 10^-4 and 760 Torr respectively, and \(C\) and \(\lambda\) are the frequency constant and decay constant for O2 adsorption on SWCNTs. The fitted data are shown in Table 1 and Fig. 5b. Firstly, the purified film exhibits a greater \(C\) by one order of magnitude, indicative of a faster electronic response to O2 adsorption (faster charge transfer). Secondly, the adsorption half-lifetime of the purified sample is a factor of 3.8 shorter than that of pristine nanotubes, namely, the gas sensitivity of purified SWCNTs is faster by a factor of 3.8 (Table 1). Thirdly, clean tubes with large \(\lambda\) mean faster O2 desorption from tube surfaces, in good agreement with Fig. 5b.

In summary, the current study shows that (i) surface impurities significantly postpone the interaction of gas with nanotubes, (ii) gas adsorption–desorption is an irreversible process on pristine SWCNTs owing to chemisorbed O2, (iii) pristine SWCNTs can be in-situ purified by chemical blast, (iv) clean tubes show faster gas sensitivity by a factor of 3.8 compared with pristine SWCNTs, and

<table>
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<th>Frequency constant (C)</th>
<th>Decay constant ((\lambda))</th>
<th>Half-lifetime/s</th>
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<tr>
<td>As-made SWCNTs</td>
<td>0.01009</td>
<td>6.5 \times 10^{-3}</td>
<td>107.18</td>
</tr>
<tr>
<td>Purified SWCNTs</td>
<td>0.0367</td>
<td>2.46 \times 10^{-2}</td>
<td>28.21</td>
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(v) elimination of surface impurities reduces the tube resistance by 17% of the initial value.

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Notes and references