Electronic supplementary information:

Gas sensing improvement of carbon nanotubes by NH₄OH-flash treatment: a nondestructive purification technique

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Fig S1 SWNT film before (a) and after NH₄OH-flash treatment (b), and the corresponding EDX spectra for pristine (c) and treated-flashed samples (d).
Table S1. Selective area of EDX data.

<table>
<thead>
<tr>
<th>Percentages</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Weight%</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-L edge</td>
<td>59.26</td>
<td>23.83</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>C-K edge</td>
<td>40.74</td>
<td>76.17</td>
<td>99.96</td>
<td>99.99</td>
</tr>
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</table>
Fig S2 Raman (a), and TGA (b) profiles of treated and untreated SWNT films.

In theory, two effects emerge when surface impurities are removed, firstly, band intensity decreases as a result of less contribution of C-C stretching to $E_{2g}$ and $A_{1g}$ modes, and secondly, the $I_D/I_G$ ratio is reduced. In practice, nanotubes purified by conventional oxidative process always exhibit an $I_D/I_G$ increase because tube structure is damaged and defect-induced phonon is enhanced at M and K points of Brillouin zone. In our raman data (a, Fig S2), intensity of both D- and G-bands is reduced after purification, confirming removal of non-graphitic surface carbons. Interestingly, the $I_D/I_G$ ratio also decreases (0.254 for pristine and 0.117 for purified), indicating that current technique is a nondestructive method. The radial breathing mode (RBM) of SWCNTs is sensitive to excitation energy, material density and temperature, particularly RBM has been used to assign the tube chirality. Our samples were measured at room temperature by 514 nm excitation wavelength and two RBM components assigned as 117 cm$^{-1}$ and 150 cm$^{-1}$, and 138 cm$^{-1}$ and 159 cm$^{-1}$, are present in pristine and purified respectively (insert). Peak at 117 cm$^{-1}$ is associated with atomic displacement in opposite direction along tube axis, which is normally suppressed by radial resonance. For as-made sample, strong peak at 117 cm$^{-1}$ (= 2.1 nm) is attributed to confinement of radial resonance by surface carbons so C-C in-plane displacement is enhanced. This is true because the 117 cm$^{-1}$ peak is
weakened upon elimination of surface impurities (i.e. purified samples). Additional peak centered at 138 cm$^{-1}$ has been previously observed and its origin remains unclear.$^4$ The peaks centered at 150 cm$^{-1}$ (as-made) and 159 cm$^{-1}$ (purified) correspond to $(11,11) = 1.65$ nm and $(17,0) = 1.56$ nm.$^5$

TGA data is shown in Fig S2 (b). Weight loss at region A (0-400°C) mainly arises from removal of moisture and small quantity of surface impurities, which is 1% and 5% for NH$_4$OH-flash treated (red) and untreated (dark) samples respectively; the smaller weight loss verifies the less quantity of surface carbonaceous materials (red). Weight increase due to oxide formation (Fe$_2$O$_3$ or Fe$_3$O$_4$) normally appears above 500 °C,$^6$ whereas, treated sample exhibits a small weight increase at 200 °C (red). This is due to the fact that elimination of surface amorphous carbons by NH$_4$OH-flash treatment has exposed embedded Fe clusters therefore oxide forms at lower temperature. At region B (400-700°C), the primary oxidation occurs at 515 °C and 450°C for treated and pristine samples respectively; the former is consistent with nanotube oxidation and the latter implies that pristine SWCNTs previously oxidized at region A (400 °C) still contains considerable quantity of surface impurities. At region C, the residual weight due to oxide formation is 23% and 15% for pristine and treated samples respectively; the lower Fe content again confirms less catalytic
particles in treated SWCNTs. It is noteworthy that lines intercepted with TGA curves at 450 °C and 515 °C at region B correspond to 9 %, similar to gap between residual weights of both samples (23 % – 15 % = 8 %). This means that oxide formation (weight increase) competes with nanotube oxidation (weight loss) at region B, which explains why pristine sample shows slower oxidation rate at region B relative to treated sample. In contrast, nanotube oxidation prevails in treated SWCNTs at region B because Fe content is lower, hence a faster oxidation rate. Lower Fe content in treated sample accounts for completion of oxide formation at lower temperature (680 °C) compared with pristine nanotubes at 710 °C.
References

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