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## Electronic supplementary information:

# Gas sensing improvement of carbon nanotubes by $NH_4OH$-flash treatment: a nondestructive purification technique

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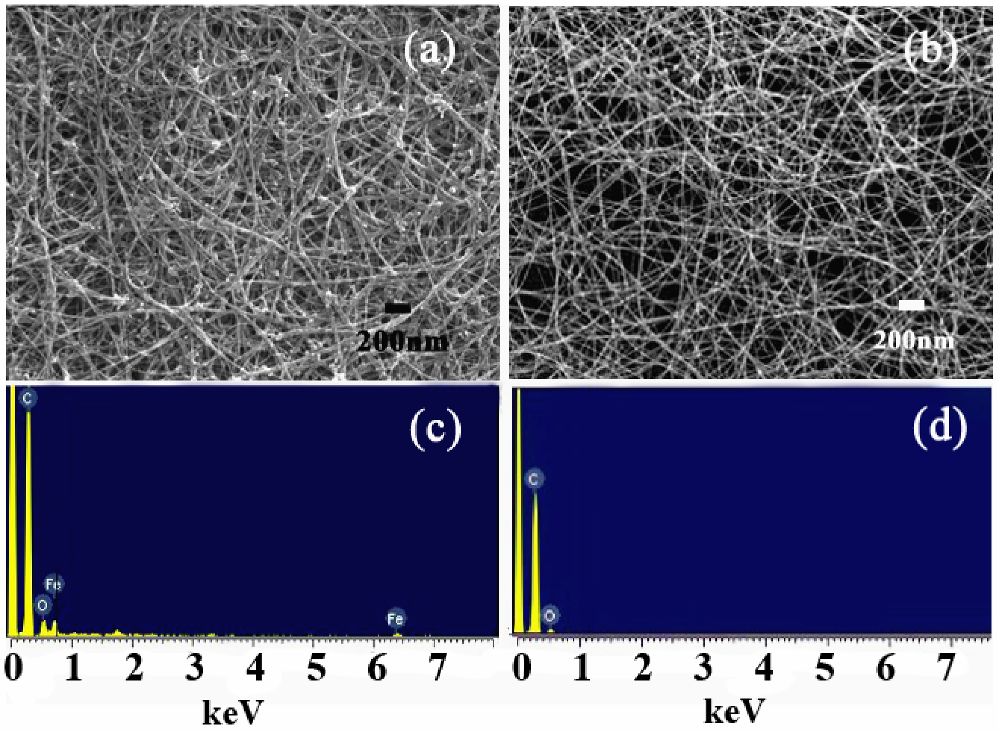
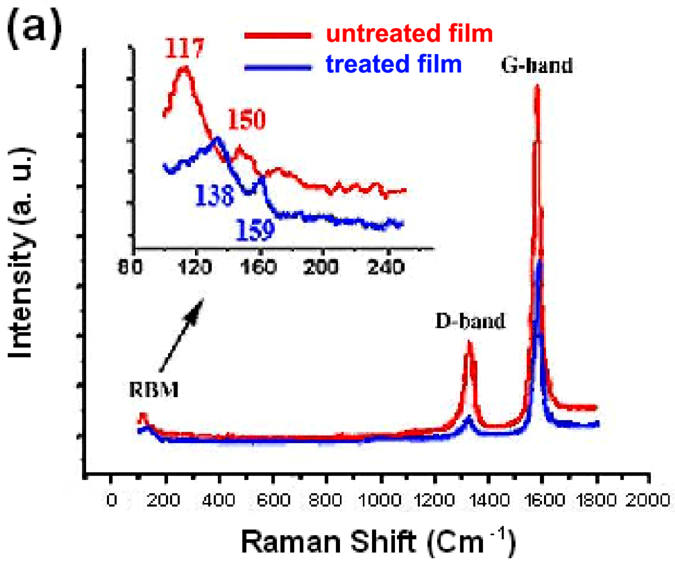


**Fig $S_1$** SWNT film before (a) and after $NH_4OH$-flash treatment (b), and the corresponding EDX spectra for pristine (c) and treated-flashed samples (d).

**Table S1**. Selective area of EDX data.

| | Pristine SWNTs | | Purified SWNTs | |
|---|---|---|---|---|
| Percentages | Weight % | Atomic % | Weight% | Atomic % |
| Fe-L edge | 59.26 | 23.83 | 0.04 | 0.01 |
| C-K edge | 40.74 | 76.17 | 99.96 | 99.99 |



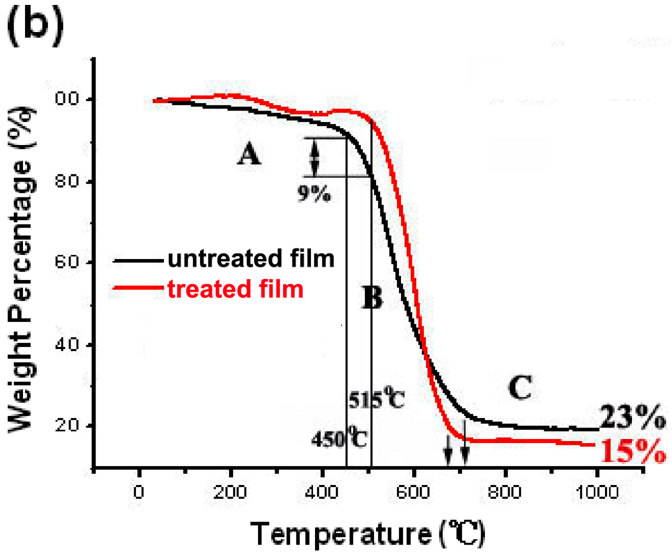


**Fig $S_2$** Raman (a), and TGA (b) profiles of treated and untreated SWNT films.

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.[1] 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 .[2] In our raman data (a, Fig $S_2$), 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.[1] 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 .[3] 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 $S_2$ (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 $NH_4OH$-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 ($Fe_2O_3$ or $Fe_3O_4$) 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 $NH_4OH$-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

1 R. G. Lacerda, A. S. Teh, M. H. Tang, K. B. K. Teo, N. L. Rupesinghe, S. H. Dalal, K. K. K. Koziol, D. Roy, G. A. J. Amaratunga, W. I. Milne, M. Chhowalla, D. G. Hasko, F. Wyczisk, and P. Legagneux, *Appl. Phys. Lett.*, 2004, **84**, 269.

2 S. Bandow, A. M. Rao, K. A. Williams, A. Thess, R. E. Smalley, and P. C. Eklund, *J. Phys. Chem. B*, 1997, **101**, 8839.

3 P. Bernier, W. Maser, C. Journet, A. Loiseau, M. L. D. L. Chapelle, S. Lefrant, R. Lee, and J. E. Fischer, *Carbon*, 1998, **36**, 675.

4 A. M. Rao, E. Richter, S. Bandow, B. Chase, P. C. Eklund, K. A. Williams, S. Fang, K. R. Subbaswamy, M. Menon, A. Thess, R. E. Smalley, G. Dresselhaus, and M. S. Dresselhaus, *Science*, 1997, **275,** 187.

5 N. Braidy, G. A. Botton, and A. Adronov, *Nano Lett.*, 2002, **2**, 1277

6 P.C.P. Watts, W.-K. Hsu, H. W. Kroto, and D. R. M. Walton, *Nano Lett.*, 2003, **3**, 549.