

**Electronic Supplementary Information for
An Efficient Carbon Precursor for Gas Phase Growth of
SWCNTs**

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1. Electron microscopy observation of as grown products

All as grown products were observed by scanning electron microscope (SEM) (Hitachi, S-5000). Typical SEM images of as grown products from n-propylbenzene, styrene, allylbenzene and 1,4-divinylbenzene without addition of C₂H₄ are shown in figure S1. Very clear net like structures of CNTs can be seen here in figure S1.

Furthermore these as grown products were analyzed by transmission electron microscope (TEM) (JEOL, JEM 1010F). This analysis showed that the major part of products is composed of SWCNTs. Typical TEM images of abovementioned products are shown in the inset of figure S1.

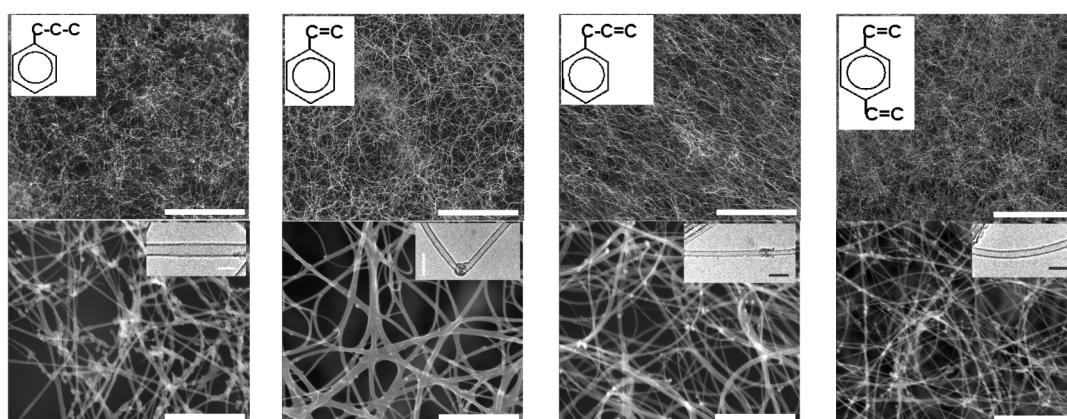


Figure S1. SEM images of as grown products from aromatic hydrocarbons n-propylbenzene, styrene, allylbenzene and 1,4-divinylbenzene (left to right respectively) showing clear net work of CNTs. Scale bars for upper and lower rows are 3 μ m and 300nm respectively. SEM observations of as grown products from toluene, p-xylene, ethylbenzene, n-propylbenzene, styrene, allylbenzene and 1,4-divinylbenzene on addition of 5.0 sccm C₂H₄ were also performed confirming a clear net work of CNTs similar to these. In the inset of lower row, TEM images of as grown products are shown (scale bars are 4, 10, 10, 5 nm respectively) which clearly show that produced CNTs are SWCNTs.

2. Characterization of as grown products by resonance Raman measurements

Resonance Raman analyses were performed for as grown products from all hydrocarbons in both cases which can be seen in figure 2 in the main text. Appearance of radial breathing mode (RBM) peaks also clearly support the production of SWCNTs. For detail information, Table 1 shows the ratio of peak intensities of the tangential mode (G-band) and the disorder induced mode (D-band), RBM peaks positions, and corresponding diameters calculated by using the experimental relationship, $d = 248/\omega_{\text{RBM}}$ (Jorio *et al.*, Phys. Rev. Lett. **86**(2001)1118), where ω_{RBM} is observed RBM's vibration frequency and d is the tube diameter.

As shown in Table S1, appearance of RBM peaks towards higher wave number in each hydrocarbon after addition of C₂H₄ was observed. For example, the RBM peak of SWCNTs produced from styrene (black line "e" in figure 2) without addition of C₂H₄ were observed at wave

number 116 cm^{-1} that can be assigned to diameter of 2.14 nm, while after addition of C_2H_4 (grey line “E” in figure 2) RBM peaks of SWCNTs were observed at wave numbers 145 and 186 cm^{-1} that can be assigned to the diameters 1.71 and 1.33 nm, that means production of relatively narrower SWCNTs. Similar trend in appearance of RBM peaks towards higher wave number can be seen in the two columns of Table S1 from top to bottom, that is, observed RBM peak positions of produced SWCNTs from n-propylbenzene to 1,4-divinylbenzene without addition of C_2H_4 (black lines, d-g in figure 2), and from toluene to 1,4-divinylbenzene on addition of C_2H_4 (grey lines A–G in figure 2).

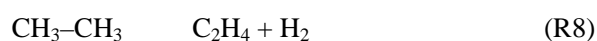
In conclusion of RBM analysis, similarity in the trend of RBM peaks indicates the order of production of $\text{sp}^2\text{ C}_2$ species from those hydrocarbons and finally the importance of $\text{C}_2\text{H}_3/\text{C}_2\text{H}_4$ as effective carbon precursors in the CVD growth of SWCNTs.

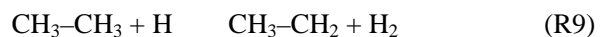
Table S1. Detailed analysis of resonance Raman spectra of as grown products

Name of used hydrocarbons	Without addition of C_2H_4			On addition of C_2H_4		
	G/D ratio	RBM peaks positions (cm^{-1})	Diameter (nm)	G/D ratio	RBM peaks positions (cm^{-1})	Diameter (nm)
Toluene				271	96	2.58
p-xylene				197	96	2.58
Ethylbenzene				158	113	2.19
n-Propylbenzene	185	96, 103	2.58, 2.41	189	116	2.14
Styrene	157	116	2.14	201	145, 186	1.71, 1.33
Allylbenzene	192	117	2.12	214	119, 145	2.1, 1.71
1,4-divinylbenzene	232	134, 186	1.85, 1.33	187	149, 186	1.66, 1.33

3. Cause of Enhancement in yield from toluene to ethylbenzene

In particular, the trend of enhancement in yields from toluene to ethylbenzene seems to follow the order of ease-of-production of methyl radicals from them. Since these hydrocarbons didn't produce SWCNTs without the addition of C_2H_4 , this interesting trend suggests that methyl radicals also contribute to C_2H_4 production as a result of chemical reactions. Possible low energy reaction routes include the quick dimerization of methyl radicals to produce ethane (R7) as well as addition with hydrogen to form methane. Latter ethane can produce ethylene by the direct dehydrogenation (R8) or by hydrogen abstraction (R9, R10).





To favour reactions (R7–10), another set of experiments were performed with high flow-rates of toluene, *p*-xylene and ethylbenzene without the secondary carbon source, C₂H₄. As expected, they could also produce SWCNTs. SWCNT growth from methane¹ and from ethane² might follow reactions (R7-10) and not direct decomposition into C and H₂.

References

1. J. Kong, A.M. Cassel, and H. Dai, *Chem. Phys. Lett.*, 1998, **292**, 567.
2. M.G. Donato, G. Messina, C. Milone, A. Pistone, and S. Santangelo, *Diamond Relat. Mater.*, 2008, **17**, 318.