Electronic Supplementary Material (ESI) for RSC Advances

Electronic Supplementary Information

Facile diameter control of vertically aligned, narrow single-walled carbon nanotubes

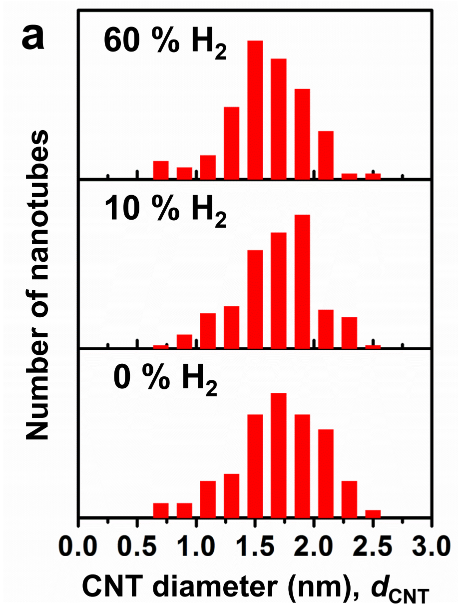
Seul Ki Youn,[a] Nuri Yazdani,[a] Jörg Patscheider[b] and Hyung Gyu Park*[a]

[a] Nanoscience for Energy Technology and Sustainability, Department of Mechanical and Process Engineering (D-MAVT), ETH Zürich, Sonneggstrasse 3, Zürich, Switzerland

[b] Laboratory for Nanoscale Materials Science, EMPA-Materials Science and Technology, Überlandstrasse 129, Dübendorf, Switzerland

*To whom correspondence should be addressed: parkh@ethz.ch

Fig. S1. (a) Negligible effect of H_2 on the nanotube diameter distribution during the CVD process and **(b)** optimized CVD process for the continuous and pulsed growths of SWNT forests. For the ultrathin Fe catalysts used in this study, the growth condition was chosen without H_2 addition. We did not observe a significant difference in the nanotube diameter distribution between CNTs grown from the pure C_2H_2 condition and the C_2H_2/H_2 condition. We interpret that C_2H_2 is a very reactive gas, a source of C as well as H_2, negating somehow the need of H_2. However, growth rate continued to decrease with H_2 vol%. This decrease in the growth rate hints that a large concentration of surface adsorbed hydrogen may inhibit the generation and/or adsorption of carbon building blocks. In addition, prolonged H_2 exposure could not only reduce the iron oxide but also promote the agglomeration of the Fe catalyst layer and the catalyst coarsening.



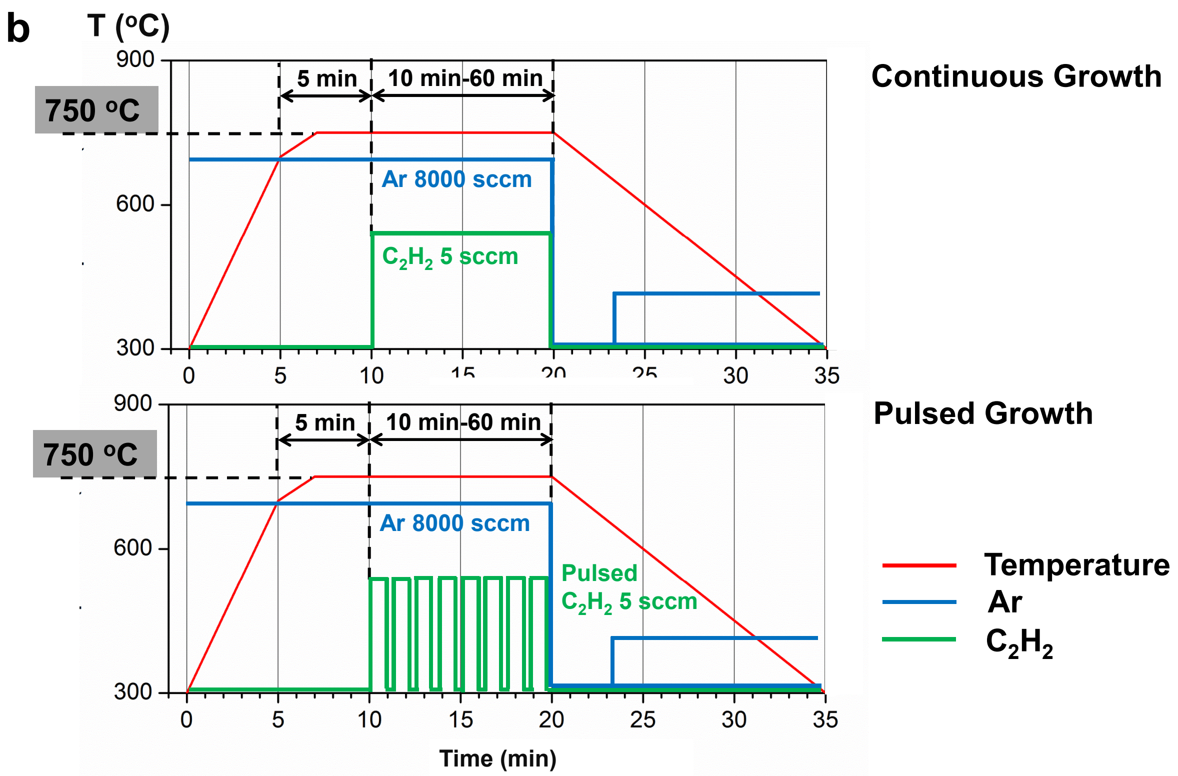
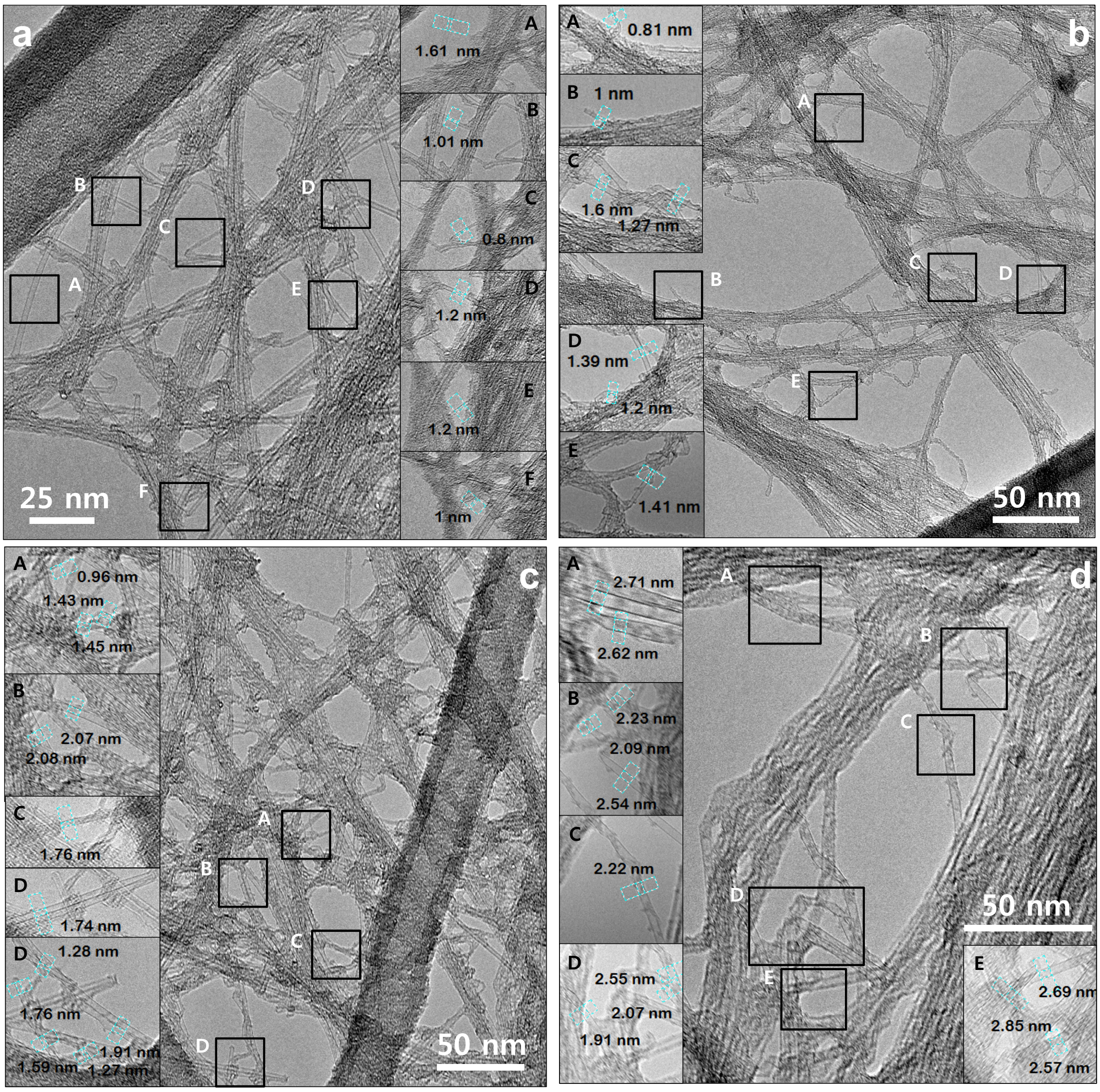
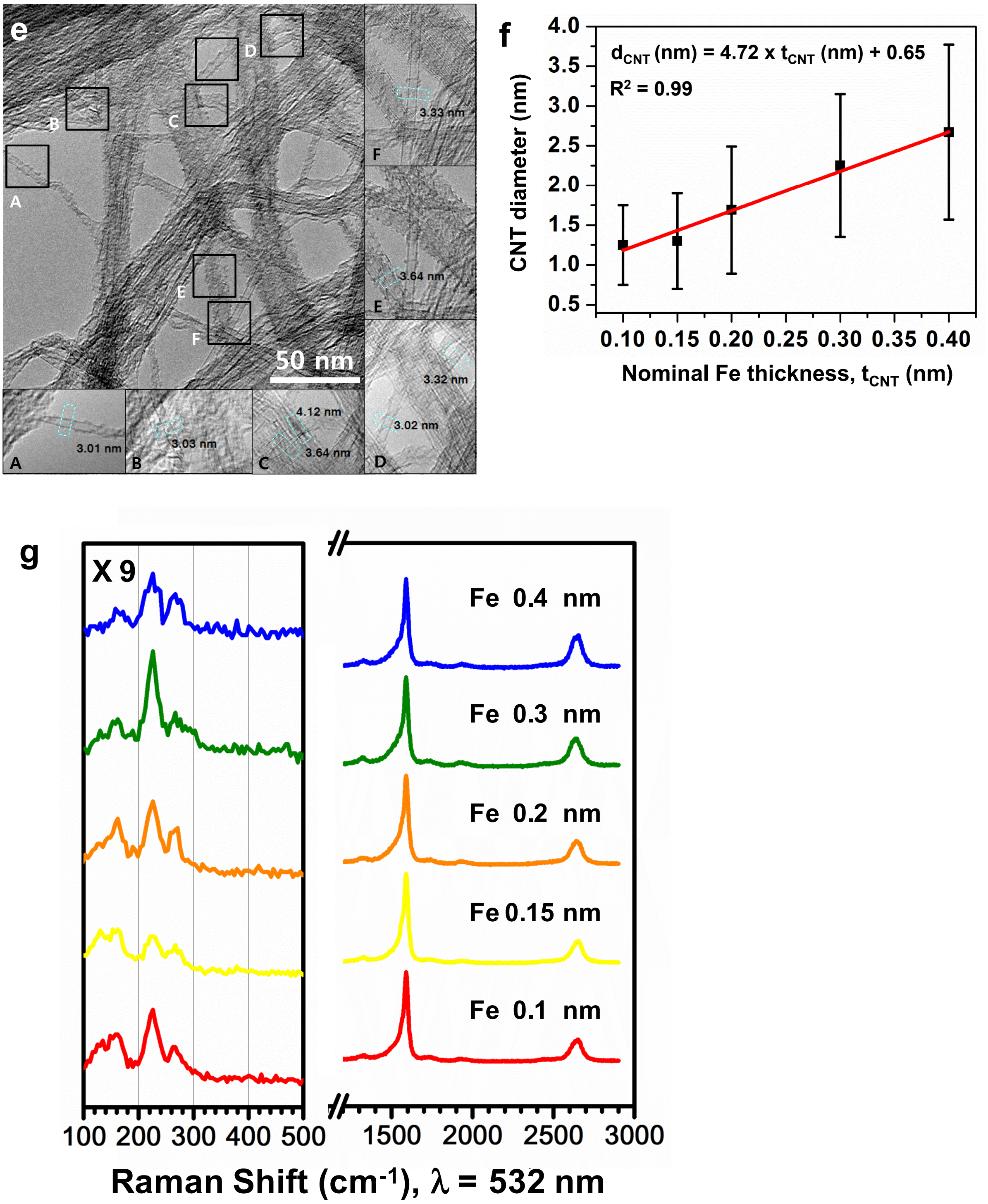
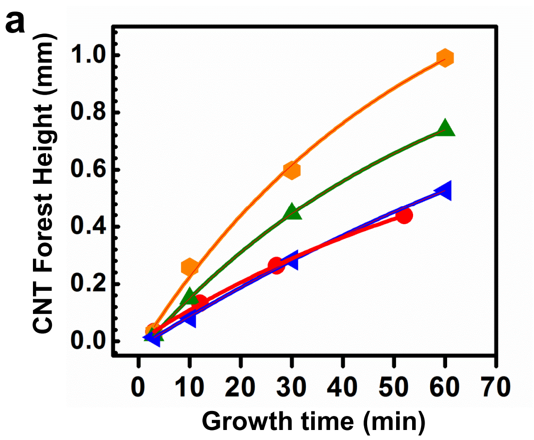


Fig. S2. HR-TEM images of SWNTs grown from ultrathin Fe catalysts with various thicknesses: **(a)** 0.1 nm, **(b)** 0.15 nm, **(c)** 0.2 nm, **(d)** 0.3 nm, and **(e)** 0.4 nm. The nanotubes were grown at 750 °C and 70-80 mbar using Ar/C_2H_2 (8000:5 sccm) for 10 min and sampled for comparison. Plot of SWNT mean diameter as a function of the Fe layer thickness is shown in **(f)**. Additional Raman spectra using 532-nm excitation are provided in **(g)**.




e
A
B
C
D
E
F
50 nm
3.01 nm
3.03 nm
4.12 nm
3.64 nm
3.02 nm
3.32 nm
3.64 nm
3.33 nm
f
d_CNT (nm) = 4.72 x t_CNT (nm) + 0.65
R^2 = 0.99
CNT diameter (nm)
Nominal Fe thickness, t_CNT (nm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.10
0.15
0.20
0.25
0.30
0.35
0.40
g
X 9
Fe 0.4 nm
Fe 0.3 nm
Fe 0.2 nm
Fe 0.15 nm
Fe 0.1 nm
100
200
300
400
500
1500
2000
2500
3000
Raman Shift (cm-1), λ = 532 nm



b **Monomolecular growth fit**

$$h = A\,(1 - e^{-t/\tau})$$

Fe thickness (nm)	A	1/τ
0.1	0.87	0.01340
0.2	1.48	0.01869
0.3	1.19	0.01665
0.4	1.58	0.00697

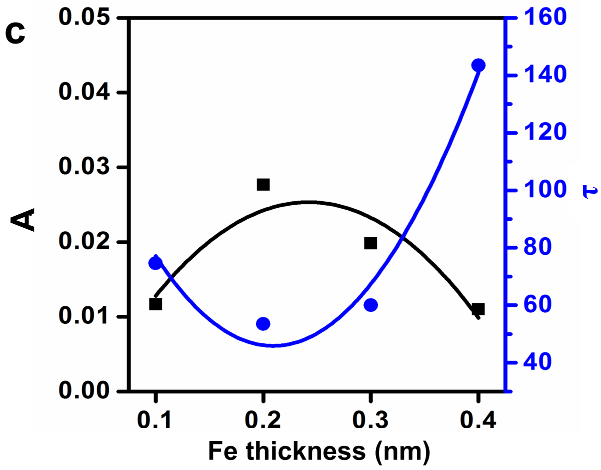


Fig. S3. (a) Time dependent growth kinetic curves represented by the heights (h) of SWNT forests grown from the catalysts of various Fe thicknesses: 0.1 (red), 0.2 (orange), 0.3 (green) and 0.4 nm (blue) **(b, c)** Monomolecular fitting parameters for the growth curves, $h = A(1 - e^{-t/\tau})$, where A (black) and τ (blue) are asymptotic height and time constant, respectively. Lines are drawn for visual guidance.

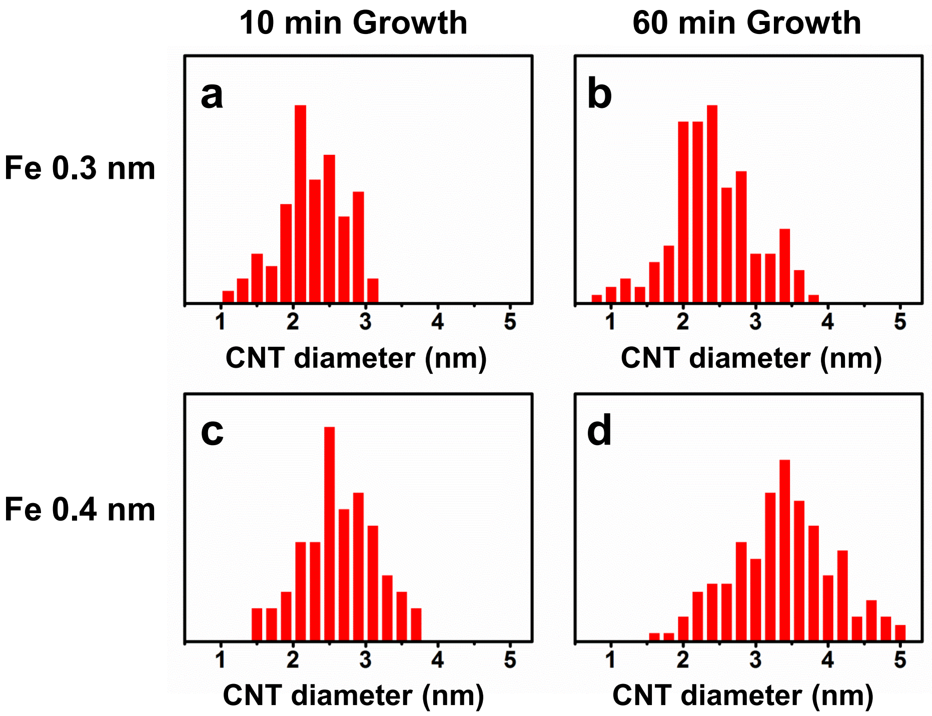


Fig. S4. TEM diameter histograms of SWNTs grown from the ultrathin Fe catalysts (>0.2 nm) for different durations. **(a, b)** Diameters of SWNTs grown from 0.3-nm-thick Fe catalysts on 20-nm-thick Al_2O_3 with growth time of **(a)** 10 min and **(b)** 60 min. **(c, d)** Diameters of SWNTs grown from 0.2-nm-thick Fe catalysts on 20-nm-thick Al_2O_3 catalysts with growth time of **(c)** 10 min and **(d)** 60 min.

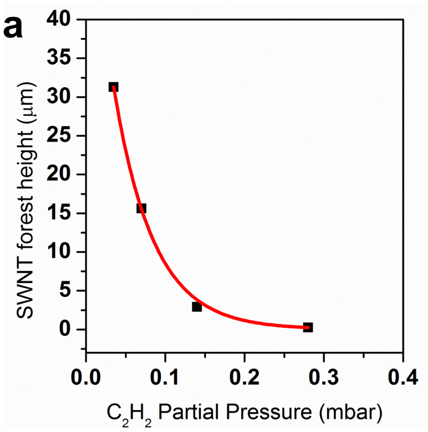


Fig. S5. P_{C2H2} dependence of average heights (growth time: 3 min) of the SWNT forests obtained from 0.2-nm-thick Fe catalysts, with an exponential fit: $h \propto \exp(-P_{C2H2}/P^*)$, where P^* is a characteristic decay constant equal to 0.051 mbar.