Supporting Information

Direct Correlation of Carbon Nanotube Nucleation and Growth with the Atomic Structure of a Re Nanocatalyst Stimulated and Imaged by the Electron Beam

Kecheng Cao,[†] *Thomas W. Chamberlain,* [‡,§] *Johannes Biskupek,*[†] *Thilo Zoberbier,*[†]

Ute Kaiser[*,†] *and Andrei N. Khlobystov*[*,‡,∥]

[†]Electron Microscopy of Materials Science, Central Facility for Electron Microscopy, Ulm University, Albert-Einstein-Allee 11, Ulm 89081, Germany

[‡]School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

[§] Institute of Process Research and Development, School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom

[∥] Nanoscale & Microscale Research Centre (nmRC), University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

E-mail: ute.kaiser@uni-ulm.de; Andrei.Khlobystov@nottingham.ac.uk

AC-HRTEM image with a large field of view

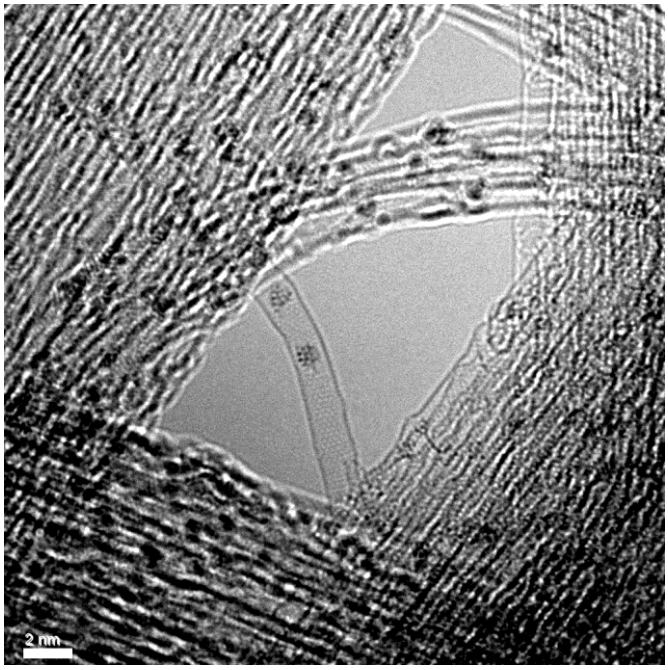

Figure S1. AC-HRTEM image of Re@SWNT (0 s image of Supplementary video 1) with a large field of view showing the wider environment of the Re nanocluster which catalyzed the growth of the SWNT.

Detailed AC-HRTEM time series of the Re nanocluster catalyzing the growth of a SWNT

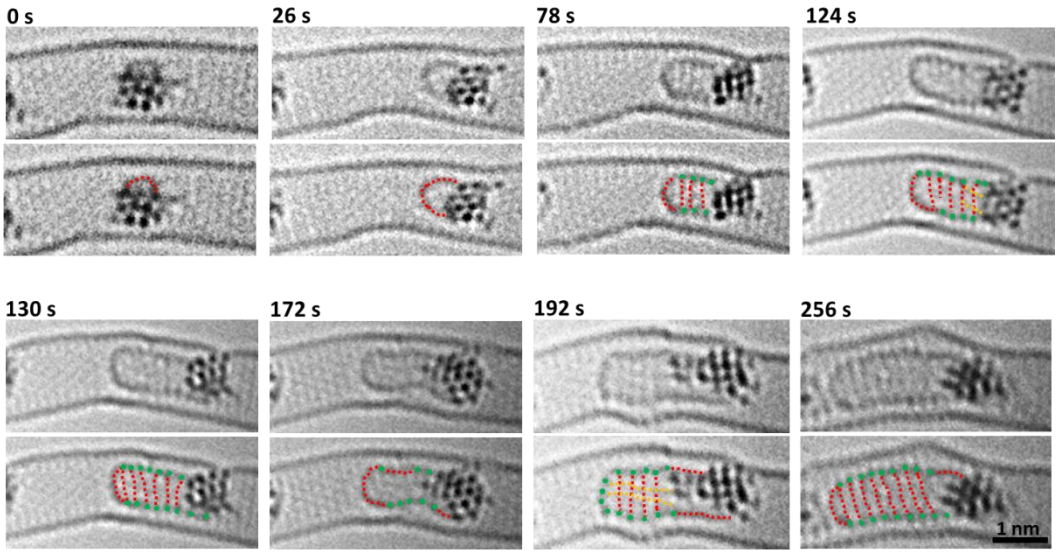

Figure S2. From 0 s to 26 s, the cap of the SWNT is formed. From 78 s, the lattice structure of the newly formed SWNT can be observed. At 256 s, the well-defined lattice structure confirms the formation of SWNT with the green spots marking discrete, distinguishable carbon atoms of the newly formed SWNT. The red and

yellow dashed lines denote the distinguishable lattice structure of the SWNT.

Determination of the chiral index of the newly formed SWNT

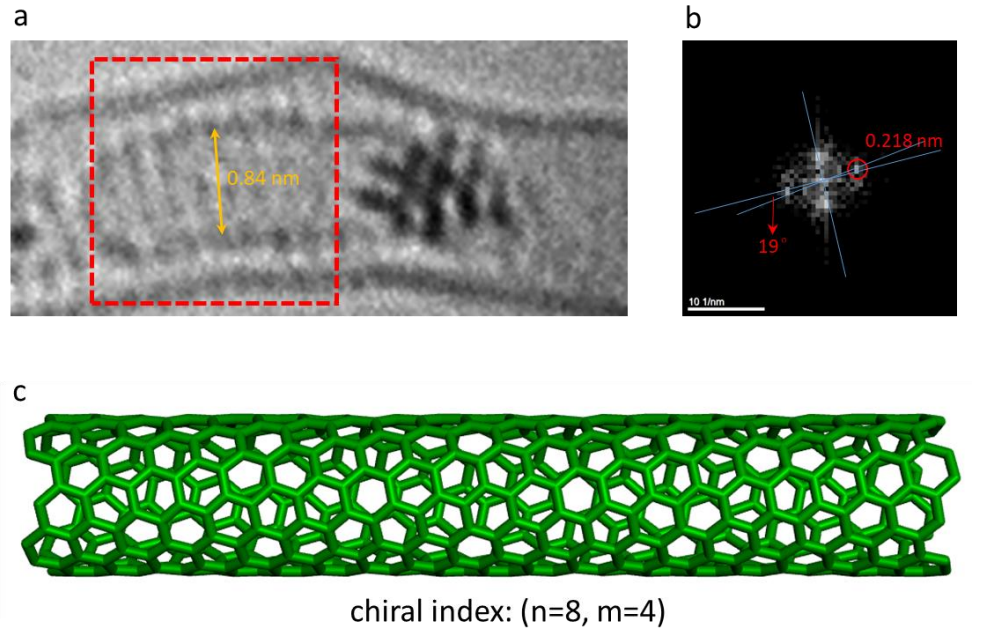

Figure S3. Fast Fourier transformation (FFT) of the framed area in a) for the newly formed SWNT is shown in b). The chiral index of the newly formed SWNT is determined by measuring the diameter of the SWNT (0.84 nm) and the characteristic FFT signal. The chiral index of the SWNT is n = 8 and m = 4. A model of the SWNT structure is shown in c).

Stability of Re cluster confined in SWNT under e-beam irradiation

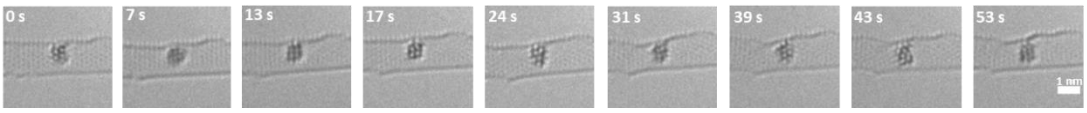

Figure S4. Time-series AC-HRTEM images showing a relatively stable Re cluster only changing its structure slightly over the course of 40 seconds, with no evidence of single Re atom ejection under 80 keV e-beam irradiation with a dose rate of 1×10^6 $e^-/nm^2 \cdot s$.

A crystalline Re cluster with a diameter of ~1 nm is confined in a SWNT. During the following 40 seconds' e-beam irradiation, no catalytic reaction between this Re cluster and the host SWNT is triggered by the e-beam. The crystalline Re cluster is relatively stable compared with the labile Re cluster shown in the time series in the main text. The maximum kinetic energy transferred from 80 keV electrons to Re atom is 1.02 eV

while the cohesive energy of bulk Re metal is 8.03 eV. Although the cohesive energy of a Re atom on the surface of the small Re cluster is expected to be lower, the 80 keV electrons are not able to directly sputter such Re atoms from the small Re cluster prior to an initial cluster/nanotube reaction triggered by the electron beam. Thus, we demonstrate it is the catalytic reaction between the Re cluster and the host SWNT that is required to make the structure of the Re cluster more flexible and dynamic, and it is this resultant, flexible structure that is able to release dynamic single Re atoms, which in turn promotes the catalytic reaction of carbon nanostructure growth.

Defect healing by lattice reconstruction

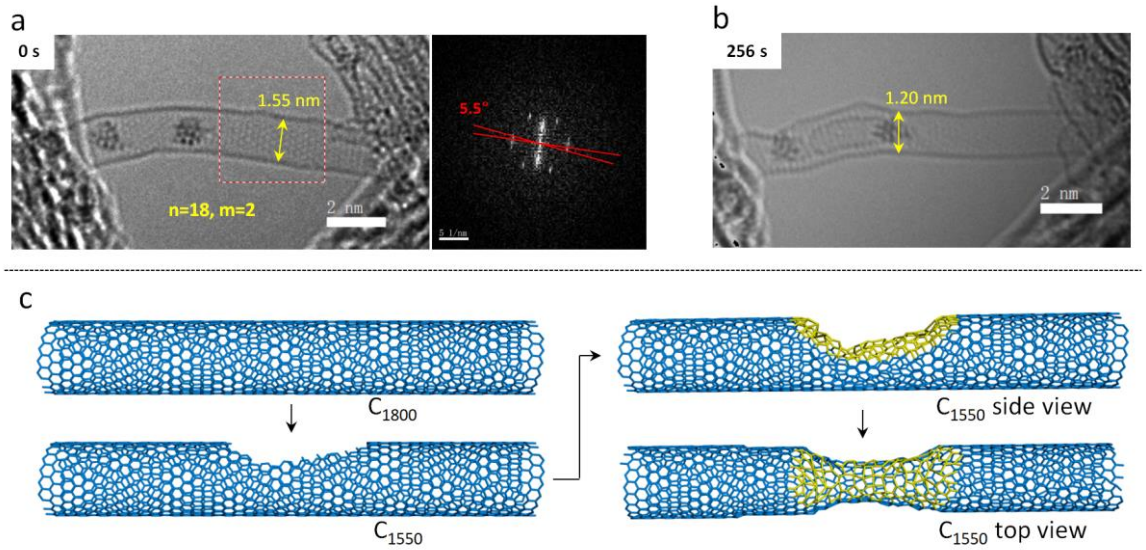

Figure S5. a) The chiral index of the host SWNT is determined to be (18, 2) by measuring its chiral angle from FFT and diameter. b) The diameter of the deformed host SWNT decreased from 1.55 nm to 1.20 nm. c) Simulated models showing the influence of losing 250 carbon atoms from a SWNT containing 1800 carbon atoms. The defect can be healed by reconstruction which would lead to a deformation highlighted in yellow.

We estimate that the number of carbon atoms needed for the formation of a new nanotube with the chiral index of (n=8, m=4) and length of 2.5 nm, i.e. the correct size and shape to fit with the original SWNT cavity shown in our study, is approximately 250 ± 20 atoms. The chiral index of the host SWNT is n=18 and m=2, as shown in Figure S5a. As illustrated in Figure S5c, the removal of 250 carbon atoms is substantial and

creates a big defect in the pristine SWNT containing 1800 carbon atoms (chiral index; n=18, m=2). However, instead of losing 250 atoms immediately, the 250 atoms lost during the processes shown in this paper are extracted by the Re clusters gradually over 256 seconds. As theoretically calculated previously, the defects in the SWNT can be 'healed' via carbon lattice reconstruction.[1-3] In our case, the gradually increasing defects are being healed at a similar rate, resulting in the deformation of the original SWNT, as shown in Figure S5b and Figure S5c.

Quantifying the degree of crystallinity of the Re cluster in the two growth stages

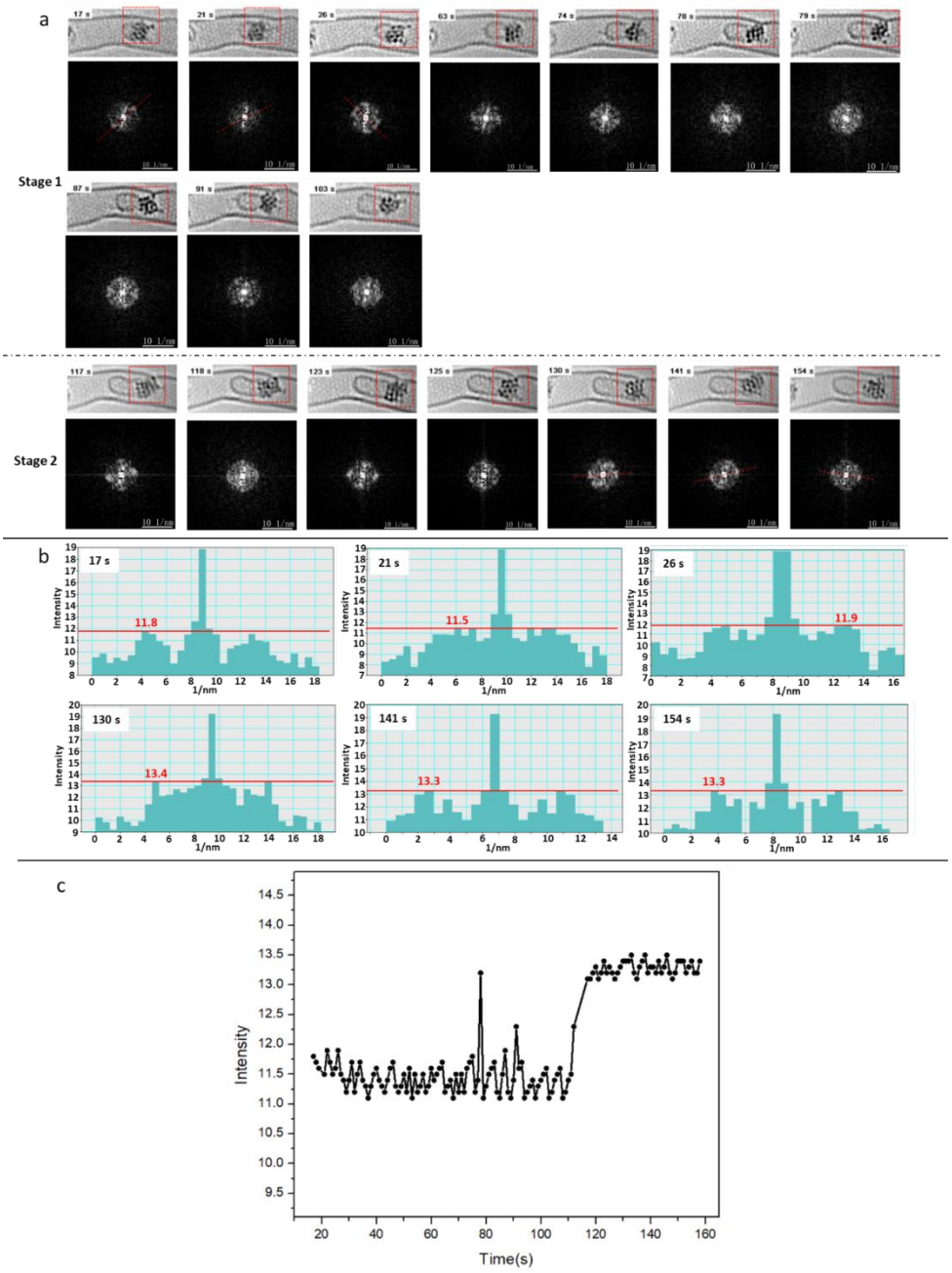

Figure S6. a) Representative HRTEM images and corresponding FFTs of the Re cluster (in the red boxes) in each frame. b) The profile lines corresponding to the red dash lines crossing the strongest 'diffraction spots' in the FFT in a) show the different crystallinities of the Re cluster in different frames. c) Plot depicting the changes in the degree of crystallinity of the Re cluster using the intensity of the FFT profile of the Re cluster in each frame of Growth Stages 1 and 2.

The degree of crystallinity of the Re cluster is quantified using the intensity of the FFTs (Fast Fourier Transforms) of the cluster in different frames of Growth Stages 1 and 2.

The FFTs of the Re cluster in the representative images of Figure 2 in the main text are shown in Figure S6a. In Figure S6b, the profile lines of the corresponding red dashed lines in the FFTs of 17 s, 21 s, 26 s, 130 s, 141 s and 154 s are presented. The intensity of the strongest 'diffraction spots' on the red dashed lines of the FFTs reflect the crystallinity of the Re cluster at each stage. The strongest 'diffraction spots' in the frames of Stage 2 show significantly higher intensity than the diffraction spots' in the frames of Stage 1. Importantly the images were collected using the same dose rates and exposure times in all cases so intensities are directly comparable. In Figure S6c, the crystallinity of the Re cluster, represented using the intensity of the FFT spot for every frame in Stage 1 and 2 are presented, demonstrating that the Re cluster in Stage 2 is a more stable and more crystalline structure.

Supporting references

[S1] Lee, G.-D.; Wang, C. Z.; Yoon, E.; Hwang, N.-M.; Ho, K. M. *Appl. Phys. Lett.* **2008** *92*, 043104.

[S2] Krasheninnikov, A. V.; Nordlund, K. *Appl. Phys. Lett.* **2010** *107*, 071301.

[S3] Lee, A. T.; Kang, Y.-J.; Chang, K. J.; Lee, I.-H.; *Phys. Rev. B* **2009** *79*, 174105.