

Supplementary Information

Metastable morphological states of catalytic nanoparticles –

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Figure S1 shows a series of snapshots from a real-time video recorded after the start of bamboo-like carbon nanotube (BCNT) growth from a $R = (3.2 \pm 0.1)$ nm radius Ni catalyst particle. Schematic drawings below each frame illustrate the observed changes in catalyst morphology and the BCNTs formation process. The sequence here starts from when the catalyst nanoparticle has a pear-like shape with the CNTs anchored at well-defined step edges (marked by arrows in Fig. S1a). At this point, the particle is starting its elongation. During this process, new tubes are added into the interior of the carbon structure. At the end of the approximately 6 s of elongation (Figs. S1a-c), the elongated particle has a length that is approximately three times the radius of the original particle. The outer CNT then detaches from the lower half of the particle and the particle roughly recovers its original, spherical form with the innermost tube's rim still attached to the steps (Fig. S1e). BCNTs form through the cycles of nanoparticle elongation and retraction, which occur with frequencies in the range 0.013 s^{-1} to 0.086 s^{-1}

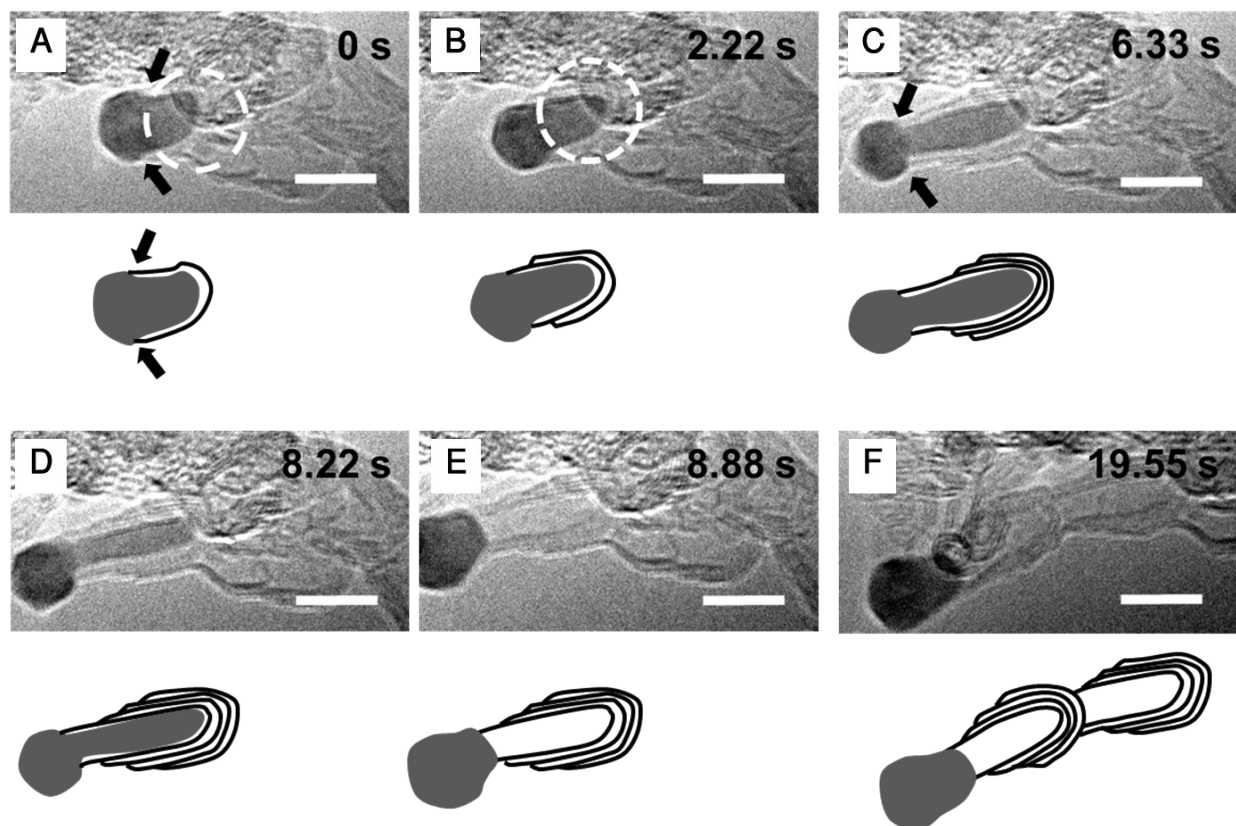


Figure S1. Snapshots from a real-time video of bamboo-like carbon nanotubes (BCNT) growth. A portion of the nickel catalyst nanoparticle ($R = (3.2 \pm 0.1)$ nm in radius) elongates inside the tubular structure during growth. When the radius of the inner tube reaches $P = (1.2 \pm 0.2)$ nm – less than half the radius of the nickel particle – the nanoparticle exits the tube and recovers its spherical shape. Schematic drawings below each frame illustrate the process, where the solid shape depicts the catalyst nanoparticle and lines the CNT. Scale bars are 5 nm. The video sequence shows: (a,b) The tubes anchor to step edges (pointed to by black arrows) and the tube caps attach to the upper half of the catalyst particle (indicated by white circles) during both the early stages of growth and elongation. (c) New steps form at the interface between the upper and lower halves of the particle, which results in a more defined interface (pointed to by black arrows). These steps provide energetically favorable sites for new nanotubes to nucleate¹, always with a conical cap, from inside the original tube with a consistent (0.34 ± 0.08) nm spacing. (d) Outer tubes detach from the particle but stay in contact with newly-formed inner tubes. (e) After the particle detaches from the cap of the inner most tube, it recovers a roughly spherical shape. (f) In the original shape, a new hemispherical carbon cap forms with the rim anchoring at the surface steps on the particle. The elongation process then repeats.

IMAGE PROCESSING METHODOLOGY

A sum total of 579 frames require analysis for the extraction of morphology descriptors defined in the main text. To address this need, we develop an algorithm that performs accurate, unbiased binarization of the image series. Figure S2 shows the image processing steps applied to a representative image of an elongated particle. A background subtraction removes low frequency non-uniformities in intensity (Fig. S2b). An “anisotropic diffusion” (Perona-Malik diffusion) smoothing then reduces image noise (Fig. S2c). This smoothing technique preserves edges, lines, and finer details important for image interpretation. This image is then thresholded to an appropriate intensity. The method then isolates the remaining noisy objects by size (units of pixels²) and eliminates them using image subtraction (Fig. S2d) to get the final binarized image.

We compute the local thickness of the particle at each pixel of the binarized image (Fig. S2e), defined as follows (http://imagej.net/Local_Thickness).² For Ω the set of all points in the particle and $\vec{p}_1$ an arbitrary point in the particle, the local thickness, $\rho(\vec{p}_1)$, is the largest circle that contains the point and is completely within the particle’s boundary,

$$\rho(\vec{p}_1) = 2 \max_{\sigma} \left(\left\{ \sigma | \vec{p}_1 \in \text{cir}(\vec{p}_2, \sigma) \subseteq \Omega, \vec{p}_2 \in \Omega \right\} \right) \quad (\text{S1})$$

Here, $\text{cir}(\vec{p}_2, \sigma)$ is the set of points inside a circle with center $\vec{p}_2$ and radius σ . From the local thickness map, we also find the radius of the largest circle, r_L , in the image (Fig. S2f), subtract this circle from the image, and obtain the average of the local thickness of the remaining fringe region. The radius of the outer region, r , is the sum of r_L and the fringe thickness. The standard deviation in the fringe thickness is taken to be the uncertainty in r (Fig. S2g). We then extract the local thickness profile along the loci of the center of these fit circles (z -axis in Fig. S2f and Fig. S3a) from each image, as well as the taper angle θ (from the slope of the thickness profile).

The length l is the sum of t and h (in Fig. S3b), where t is the distance between points O and O' . The point O' is the center of the circle fit to the tip of the elongated portion and h is the point of intersection of line c and the circle R (in Fig. S3b). The slope of the line c is $\tan \theta$. The intercept is the thickness at point E (ρ_1), the taper θ , and the radius of the outer circle r . For an outer circle centered at the origin, the points of intersection come from the equations

$$x^2 + y^2 = r^2 \quad (\text{S2})$$

and

$$y = x \tan \theta + \frac{\rho_1}{2} - r \tan \theta \quad (\text{S3})$$

We subtract the x coordinate of the point of intersection (x_i) from r to obtain h . The average radius of the elongated region (ρ) is the mean thickness value at each point along the x -axis between points ($x_i, 0$) and O' in the image. The uncertainty in ρ is the standard deviation in the thickness of the fringe elements of the elongated region, i.e., the edge variations outside of the fit circles.

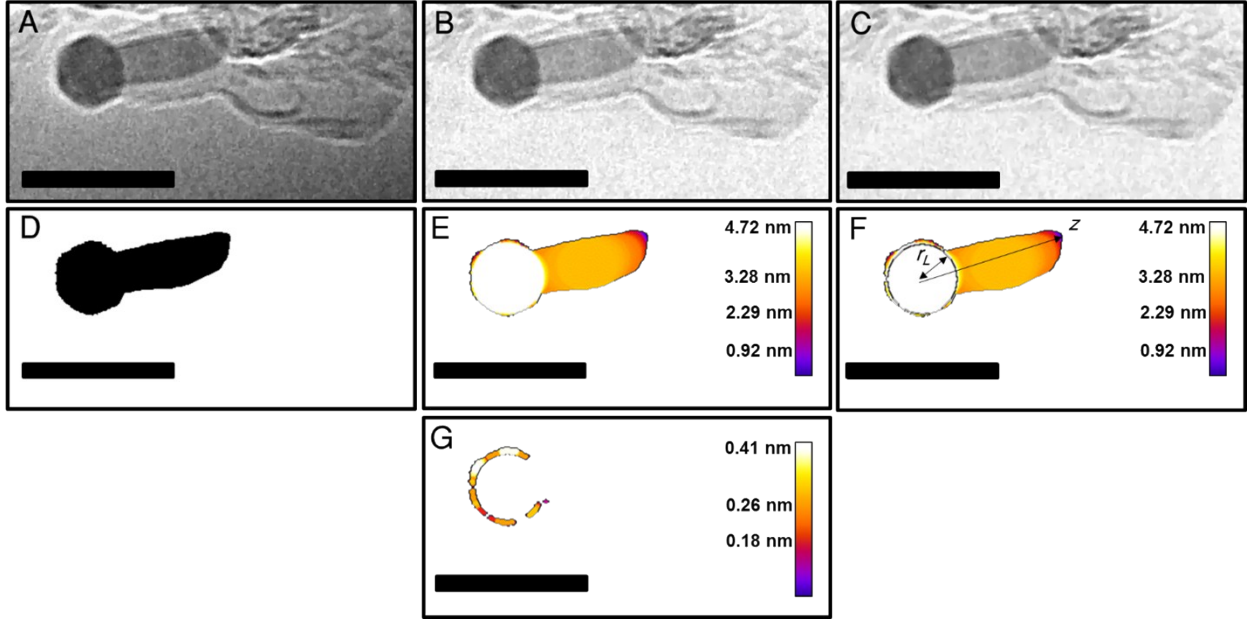


Figure S2. Image processing from a real-time video of MWCNT growth. (a) Representative time slice from the Movie S1; (b) background subtraction applied to (a); (c) anisotropic diffusion smoothing applied to (b); (d) binarization applied to (c); (e) Visual representation of the local thickness calculation applied to (d), with the thickness labeled according to the color map inset in the image; (e) Image (e) with in-circle radius (r_L) and loci of in-circle centers z indicated; (g) The local thickness map of the fringe regions of the spherical domain of the particle. Scale bars are 10 nm.

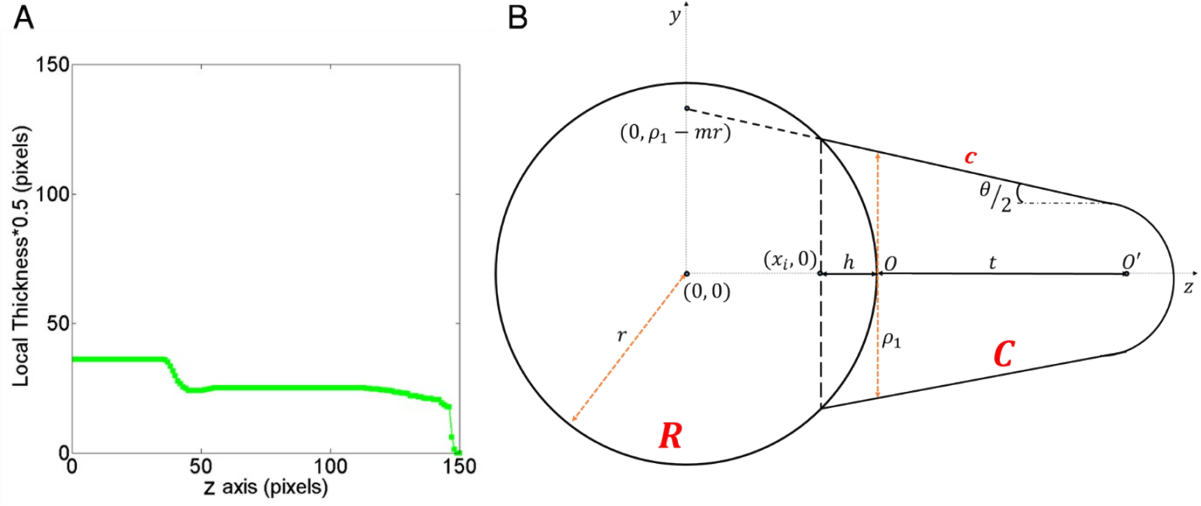


Figure S3. Example data and model. (a) The local thickness profile along the loci of the center of the fit in-circles (z -axis). (b) Schematic showing the model structure and the parameters for the computation of h . The point of intersection of the line c of slope m and intercept $(0, \rho_l - mr)$ and the circle, R , centered at the origin with a radius r is calculated. The x coordinate of this point subtracted from r gives h . The values m , r , ρ_l are measured using the analysis method shown in Fig. S2.

ADDITIONAL DATA AND IMAGES

Figure S4 shows three additional cycles with error bars extracted from the ETEM videos. Figure S5 shows a schematic of how carbon nanostructure growth proceeds for non-tapered and tapered catalytic nanoparticles. Bamboo-like structures form when the tapering is small, whereas carbon nanofibers (CNF) form when there is more substantial tapering.

Figure S6 is a series of frames from a real-time video of CNF growth from an approximately $R = 4.5$ nm Ni catalyst nanoparticle at the tip. The video sequence starts when the catalyst particle is partially elongated inside a CNF (Fig. S6a). The average ratio of elongation length to particle diameter is 0.25 ± 0.04 , which is much smaller than the smaller particle analyzed in the main text ($\approx 3\times$). The higher degree of tapering, possibly due to how the carbon cap forms, results in the shorter elongation and in CNF growth rather than BCNT growth. A more detailed analysis of the binding region and the interplay with surface energies is required to confirm that cap formation is indeed the mechanism that drives the higher degree of tapering. Kinetics also can play a role here, as larger tubes (that form on the larger nanoparticle) have a smaller variation in the rate at which they grow. When a small nested tube forms, its growth rate significantly surpasses the previous tubes growth rate, causing detachment of that larger tube. This is less likely to occur when the tube radius is large. Importantly, the scale invariance of the model in the main text demonstrates that the smaller shape changes are not due to unfavorable energetics (except potentially for the energetics/structure of rim binding).

Figure S7 shows a series of images extracted from the video of outward tapering during elongation. The free energy landscape for this breakage event is in Fig. 5b of the main text.

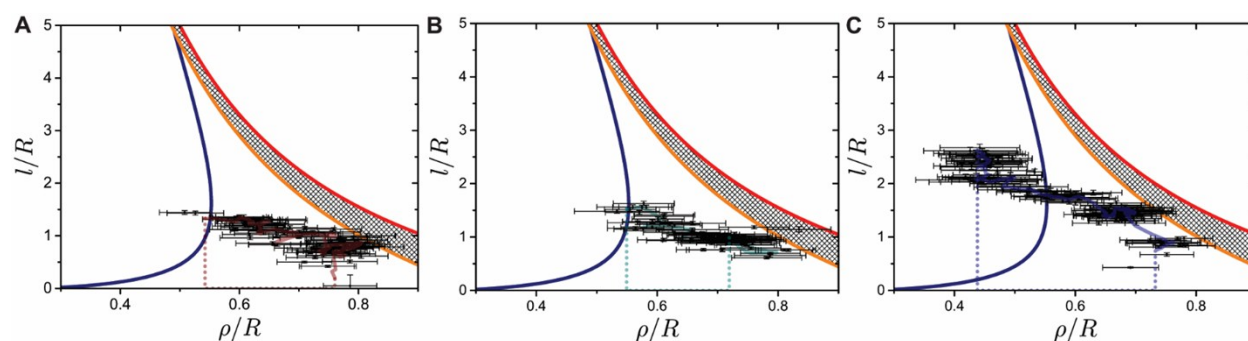


Figure S4. Three additional cycles of elongation and retraction. (a-c) These are the same plot as Fig. 3c in the main text, except for the other cycles in Fig. 3b. The carbon nanostructures are more highly tapered for these cycles, resulting in retraction at larger values of ρ/R . The blue line indicates $\Delta G = 0$ for the case $\theta = 0$ (i.e., no tapering). Above the red and orange lines are the regions where the particle is completely in the tube and where the particle would require additional faceting/restricting to elongate, respectively. The latter, in particular, would act as a barrier

to further elongation, which is seen from these trajectories – they “avoid” the orange boundary line. Error bars are plus/minus one standard deviation.

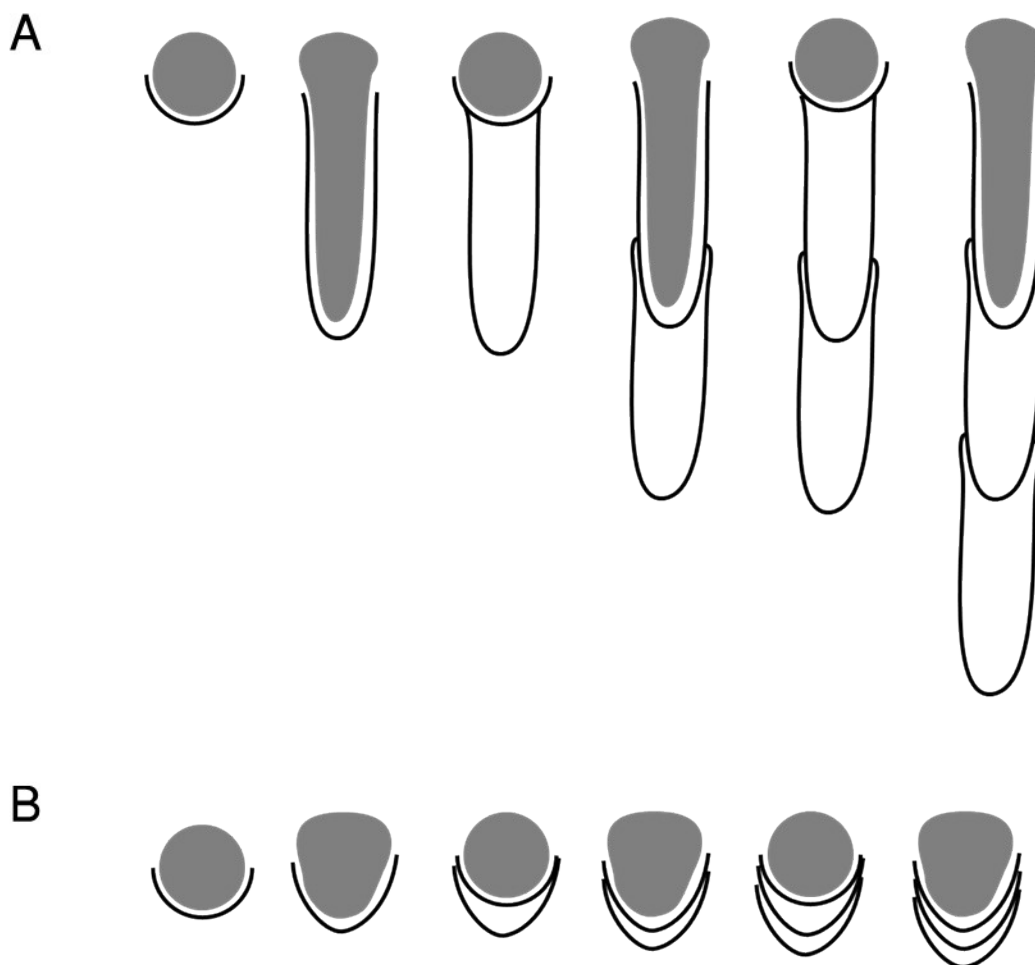


Figure S5. Schematic of carbon nanostructure formation. (a) BCNTs form when the degree of particle tapering is small. (b) CNFs form when the degree of particle tapering is large, as the latter encourages retraction to be partial and to occur at much smaller elongation lengths.

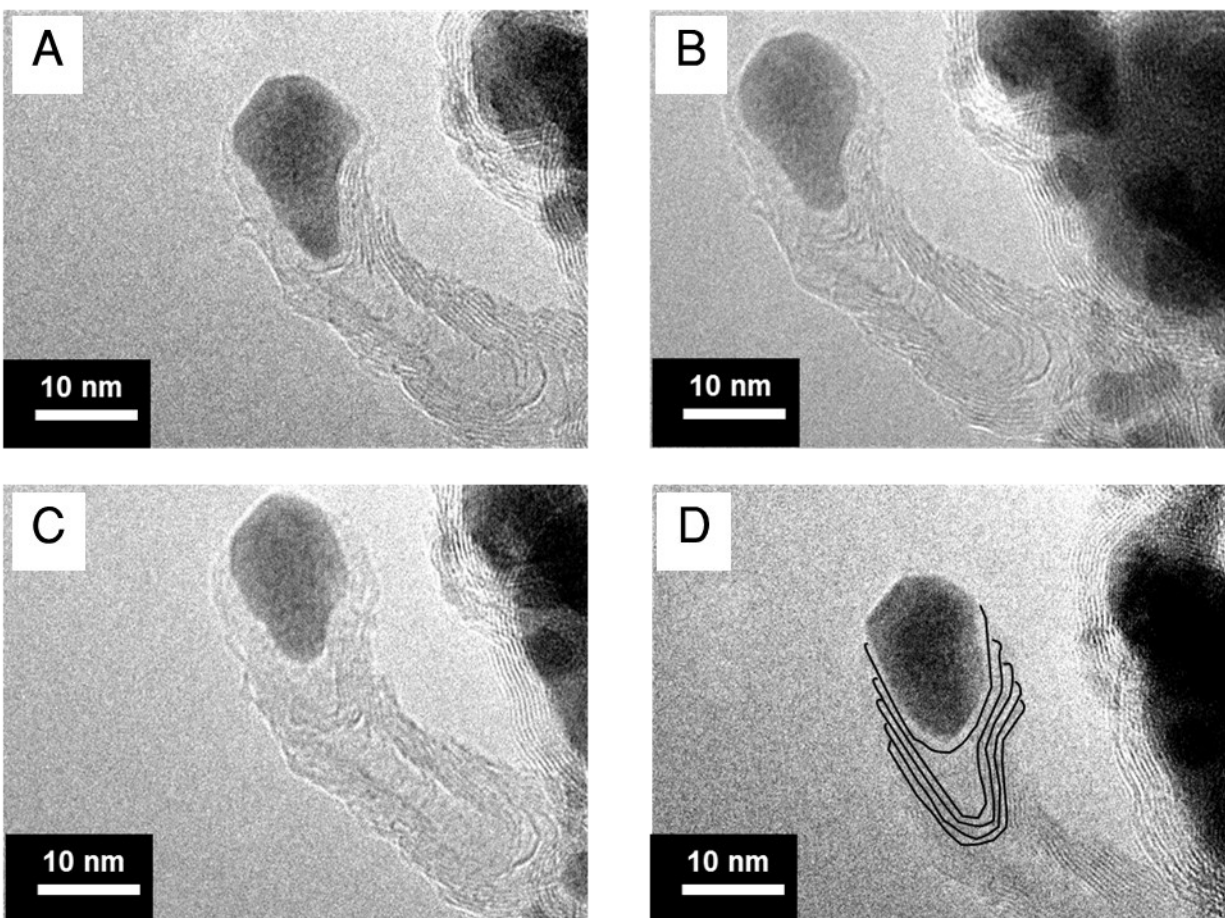


Figure S6. Frames from a real-time video of CNF growth. The ≈ 9 nm diameter Ni nanoparticle catalyst shape nearly unchanged during the CNF growth. Scale bars are 10 nm.

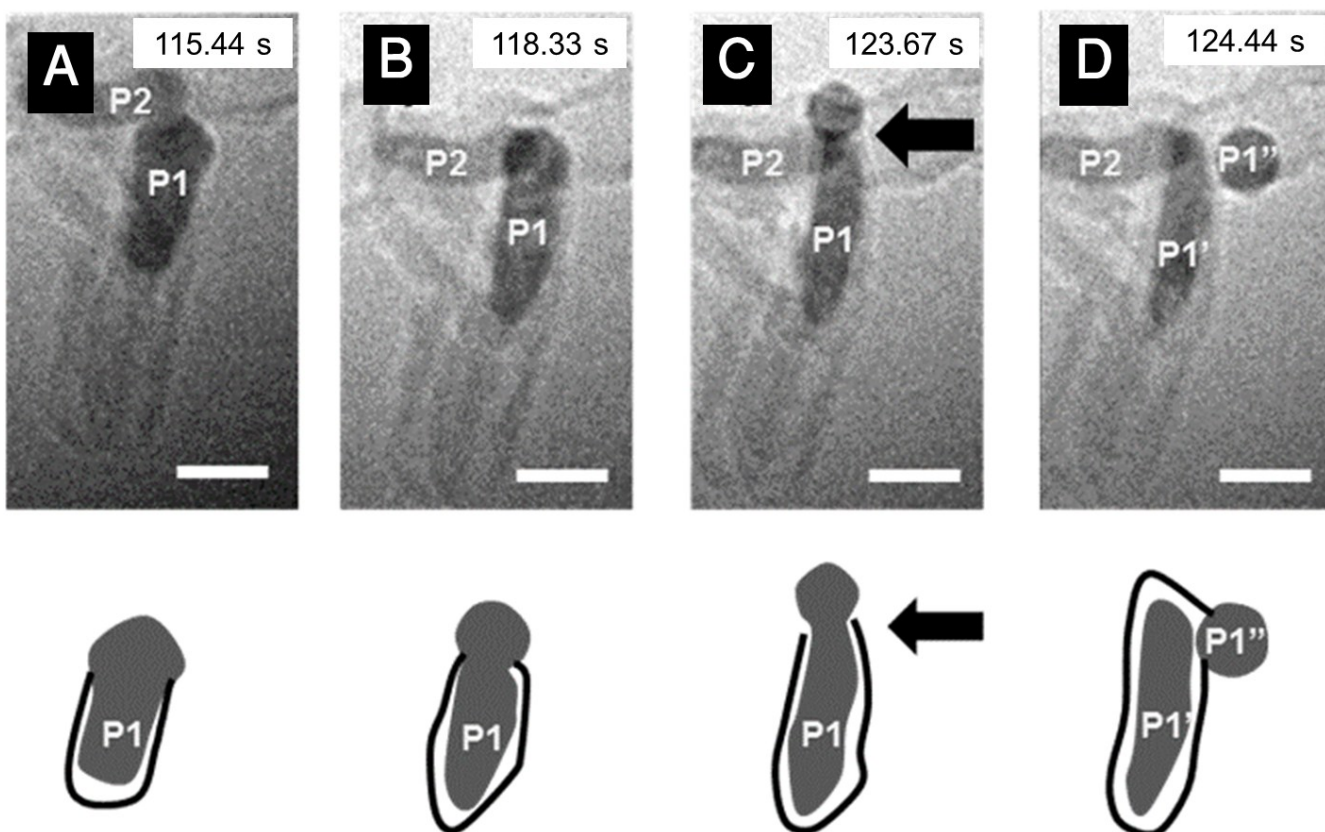


Figure S7. Snapshots from a real-time video of CNT growth. The catalyst nanoparticle (P1) elongates and then breaks into two parts (P1' and P1'') during growth. Below each frame, the schematic shows the catalyst (solid shape) and CNT (lines). Scale bars are 5 nm.

REFERENCES

1. Roth, T. A., Surface and grain-boundary energies of iron, cobalt, and nickel. *Mater. Sci. Eng.* **18**, 183-192 (1975).
2. Hildebrand, T. & Ruegsegger, P. A new method for the model-independent assessment of thickness in three-dimensional images. *Journal of Microscopy* **185**, 67–75 (1997).