

Atomic Mechanism of Metal Crystal Nucleus Formation in a Single-Walled Carbon Nanotube

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Abstract: Knowing how crystals nucleate at the atomic scale is crucial for understanding, and in turn controlling, the structure and properties of a wide variety of materials. Because of the scale and highly dynamic nature of the nuclei, however, the formation and early growth of nuclei is

1 very difficult to observe. Here, we have employed single-walled carbon nanotubes as test-tubes,
2 and an ‘atomic injector’ coupled with aberration-corrected transmission electron microscopy, to
3 enable *in-situ* imaging of the initial steps of nucleation at the atomic scale. With three different
4 metals we observed three main processes prior to heterogeneous nucleation: the formation of
5 crystal nuclei directly from an atomic seed (Fe), from a pre-existing amorphous nanocluster
6 (Au), or by coalescence of two separate amorphous sub-nanometer clusters (Re). We
7 demonstrate the roles of the amorphous precursors and existence of an energy barrier before
8 nuclei formation. In all three cases, crystal nucleus formation occurred through a two-step
9 nucleation mechanism.

10 Nucleation lies at the heart of the crystallization process and critically determines the
11 structure and size distribution of crystals, and therefore the functional properties of all materials,
12 from semiconductors to pharmaceuticals¹. The classical nucleation theory (CNT), developed to
13 elucidate the nucleation of crystals, describes crystal formation in a single step from monomers
14 (atom, ion or molecule), by attachment of individual monomers to an ordered structure
15 overcoming a single free-energy barrier.^{2,3} This can also be extended to rationalize formation and
16 nucleation of crystals through thermodynamically metastable precursors (ordered or disordered)
17 in a single step^{3,4}. However, there are a number of experimental observations which cannot be
18 satisfactorily explained using this theory, leading to the postulation of the more complicated and
19 contentious two-step nucleation mechanism (TSNM)⁵⁻¹⁰. This assembly pathway involves the
20 initial formation of an amorphous ‘precursor’ phase which is then subsequently superseded by a
21 more stable crystalline phase¹¹⁻¹⁴, or formation of stable species (ordered or disordered) which
22 never dissociate even in undersaturated conditions and can crystallize if more monomer is
23 supplied¹⁵⁻¹⁸. As a result of the two energy barriers in a TSNM, the initially formed stable or

1 metastable precursor phase can either proceed on to crystallize into a crystalline phase by
2 overcoming an additional energy barrier for crystallization or dissociate back into monomers by
3 overcoming the energy barrier for monomer detachment³.

4 A range of analytical techniques, such as X-ray diffraction^{19,20}, atomic force
5 microscopy^{3,21,22}, optical microscopy²³, are commonly applied to investigate and establish
6 different mechanisms of nucleation processes. For example, cryogenic transmission electron
7 microscopy (Cryo-TEM) allows imaging of the different nucleation stages of inorganic and
8 organic compounds, such as magnetite¹⁵, and dyes in solution²⁴, which are frozen and suspended
9 so that the nucleation processes is measured in *ex situ* discrete steps. An alternative liquid-cell
10 TEM technology enables imaging of the nucleation and growth processes of metal nanocrystals
11 (such as Au¹¹, Pt²⁵) and inorganic compounds (such as PbS²⁶) in solutions in real time with high
12 temporal and spatial resolution. Nevertheless, both the sheer volume of the liquid and the
13 material of the liquid-cell window inevitably scatter electrons during the TEM imaging process,
14 which combined with the lack of control over the location and the rate of seed nucleation, and
15 the ephemeral nature of the nucleation process, preclude the observation of the very early stages
16 of nucleation with atomic resolution. Essentially, an atomically accurate description of the
17 nucleation process is currently hindered by the fact that the critical nucleus sizes are believed to
18 fall in the range of 100-1000 atoms, which is inaccessible for atomically-resolved investigations
19 by any current analytical methods. Therefore, a conceptually new experimental approach is
20 necessary to enable direct observation of nucleation at the atomic level in real time, and to allow
21 observation to be conducted in a controlled and well-defined environment²⁷. Here we apply *in*
22 *situ* low-voltage aberration-corrected high-resolution TEM (AC-HRTEM) to study the
23 nucleation of metal crystal nucleus at the single atom level inside an electron-transparent test

1 tube, a single-walled carbon nanotube (SWNT), which possesses a well-defined atomically
2 smooth surface, and outstanding thermal, mechanical and chemical stability in different
3 conditions, including the 80 keV electron beam²⁸⁻³¹.

4 **Results and discussion**

5 **Fe crystal nuclei formed from atomic seed.** In previous works, we have demonstrated that
6 SWNTs can act as effective host-structures for extremely small (30-60 atoms) metal clusters^{29,31}.
7 In this study, we extend this approach to atomic-scale experiments that allow the observation of
8 the initial steps of the nucleation processes of γ -Fe, Au and Re crystal nucleus, at the atomic
9 level, in real time by means of low-voltage AC-HRTEM imaging. The SWNT provides an ideal
10 cavity for atom transport and a substrate for the heterogeneous nucleation of metal which
11 prevents ionization by the electron beam due to its conductive structure. Here, the electron beam
12 of the TEM is not only an imaging probe but also a stimulus for the nucleation processes by
13 transferring kinetic energy from the incident electrons to the atoms. The transferred kinetic
14 energy has a maximum value and computable distribution (Supplementary Fig. 1), and is able to
15 drive chemical reactions of molecules²⁸ and dynamics of metal clusters²⁹. In the case of metal
16 clusters, the transferred kinetic energy increases their total free-energy in a similar fashion to a
17 heating process. The increase of total free-energy can be controlled by adjusting the accelerating
18 voltage and dose-rate of the electron beam in the present experiments, thus promoting the
19 nucleation processes of metal crystallites in a similar fashion to a thermal activation. In order to
20 investigate nucleation from the most initial stages with atomic resolution, it is important to
21 obtain a fixed and observable nucleation seed with only a few atoms. As shown in Fig. 1a, a
22 cluster containing three Fe atoms located on the wall of a SWNT can serve as a nucleation seed
23 in the present experiments. During nucleation in bulk, the additional atoms or molecules are

1 delivered to the seed by random collisions, which is a thermally driven stochastic process with
2 complex mechanisms. In a SWNT the situation is significantly simplified: while the wall of the
3 nanotube provides a substrate for nucleation, mobile clusters of amorphous carbon liberated from
4 ferrocene serve as vehicles for the delivery of Fe atoms to the growing nucleus, atom by atom,
5 effectively acting as an ‘atomic injector’.

6 Amorphous carbon forms a complex with the Fe atoms (Fig. 1b, Fe atoms are indicated
7 by the rightmost red arrow), which appears to be very mobile, sliding along the nanotube cavity
8 on the timescale of a few seconds probably driven by thermal energy or electron beam excitation,
9 due to the extremely low friction of the atomically smooth SWNT³²⁻³⁴ (Section 3). High-angle
10 annular dark-field scanning TEM (HAADF-STEM) and corresponding electron energy loss
11 spectroscopy (EELS) mapping (Fig. 1c and 1d) confirm the presence of Fe in the highly mobile
12 ‘atomic injector’. The time-series AC-HRTEM images in Fig. 1e show a typical example of the
13 atomic injector in action (Section 3): stimulated by the e-beam, a cluster of iron atoms move
14 back and forth during the first 60 seconds. Due to the fact the Fe cluster is moving quickly and
15 stops at two positions in the SWNT during the exposure time of 1 second per frame, two images
16 with lower contrast (indicating partial occupancy) appear in frames at 0 s and 52 s. At 60 s, the
17 carbon cluster bonds to the Fe cluster and then translates to the right side of the SWNT in the
18 next 25 seconds.

19 The entire nucleation process of γ -Fe is successfully observed and recorded by AC-
20 HRTEM using 80 keV electrons with a dose rate of $1.4 \times 10^6 \text{ e}^- / \text{nm}^2 \cdot \text{s}$, providing a steady
21 source of energy to the atoms, with the SWNT wall acting as substrate for a nucleation seed
22 (Supplementary Video 1). The first stage (0 - 13 s, Fig. 2) shows the formation of a ‘Diatomic
23 Seed’: two Fe atoms form a pair on the outside of the SWNT wall with a distance of 0.32 - 0.34

1 nm between the metal atoms. This distance is substantially longer than the calculated equilibrium
2 bond length of 0.20 nm for an isolated Fe₂ molecule (see Section 1), and corresponds to a
3 reduction in the bond energy of the dimer from 2.2 eV (at 0.20 nm) to 0.8 eV (at 0.33 nm). This
4 demonstrates the templating role of the underlying SWNT substrate in controlling Fe-Fe distance
5 and making it more comparable to bulk γ -Fe (0.29 nm) than gas-phase Fe₂. At 8 s, the right Fe
6 atom passes through the carbon wall and enters into the cavity of the SWNT (Fig. 2c).
7 Considering that it is not possible for atoms to permeate the carbon lattice of a SWNT, the
8 observed migration of Fe indicates the presence of vacancy defects in the SWNT wall, which
9 may facilitate bonding of the Fe atoms to the SWNT. At 13 seconds, the atomic injector
10 translates along the nanotube and moves towards the diatomic seed (Fig. 2a). The consequence
11 of the interaction between the mobile atomic injector and the stationary seed becomes apparent
12 in the next sequence of events (13 - 50 s, Fig. 2b and 2c) in which the right Fe atom of the seed is
13 pushed out and the distance between the two Fe atoms is increased to 0.43 nm. The enlarged
14 interatomic distance corresponds to a reduction in the bond energy of an isolated dimer by 90%
15 to only 0.2 eV, and as such is more akin to two independent Fe atoms held apart by bonding to
16 the SWNT than an Fe₂ dimer.

17 The separation frees up space for a third atom which subsequently migrates from the
18 atomic injector into the seed at 19 s, signifying the beginning of the second stage of nucleation –
19 the ‘Atom Delivery’ process (13 - 50 s). Over the next 4 seconds, the diatomic seed grows into a
20 cluster of 17 Fe atoms (determined from image analysis in Section 7), with only one Fe atom
21 remaining in the atomic injector. The structure of the growing Fe cluster at this stage stays
22 amorphous. Metallic bonding may act as an attractive force, pulling the atomic injector towards
23 the Fe seed and holding it in place during the atom delivery stage, because after most of the Fe

1 atoms are injected (at 23 s, Fig. 2a) the remaining, relatively weak Van der Waals force is unable
2 to retain the mobile atomic injector in the vicinity of the Fe cluster and the atomic injector moves
3 away along the nanotube (50 s in Fig. 2a). The real-time imaging of the atom delivery process
4 enables the visualization of precise details of the initial stages of crystallite nucleation, showing
5 how the discrete atoms become a cluster by joining to the diatomic seed in steps.

6 At the point of atomic injector departure (50 s), a ‘Metastable Amorphous State’ stage
7 begins as the structureless sub-nanometer cluster containing approximately 17 Fe atoms
8 undergoes continuous reorganization for the next 147 seconds. During this stage, the Fe atoms
9 shuttle back and forth between the outer and inner surface of the SWNT, with the inter-atomic
10 distances and coordination numbers of Fe atoms continuously and randomly changing over time
11 (Fig. 3a). The highly dynamic nature of the metal cluster at this stage is consistent with the
12 notion of a metastable amorphous cluster, such that the positions of the constituent atoms are
13 extremely sensitive to the local conditions e.g. temperature, pressure and the local environment,
14 all of which can influence the reorganization process and therefore the final structure of the
15 crystallite nucleus. Finally, the amorphous cluster becomes ordered (at 197 s, Fig. 3a) with the
16 iron atoms adopting uniform inter-atomic distances matching the (111) plane of the γ -Fe crystal
17 lattice. This represents the fourth stage, designated the ‘Ordered Crystallite’ stage, which marks
18 the end of the nucleation process, as from this point further growth of the crystallite will be
19 strictly templated by the structure of the ordered crystal-like nucleus. The degree of atomic order
20 in the Fe cluster is elucidated by Fast Fourier Transform (FFT) analysis (second row of Fig. 3a)
21 allowing quantitative analysis of changes in the relative degree of crystallinity over time (Fig. 3b
22 and Section 6).

23

1 In the ‘Diatomic seed’ stage, interactions between the Fe diatomic seed and the SWNT
2 reduce the total free-energy of the dimer and stabilize the seed, which is similar to the
3 stabilization which occurs in heterogeneous nucleation processes where the nucleation happens
4 at the gas-solid, gas-liquid or solid-liquid interface. However, the diatomic seed is able to
5 dissociate back into discrete atoms (Supplementary Fig. 8) highlighting the metastable nature of
6 the seed and that the free energy barrier to Fe atom detachment is small for seeds of this size
7 under the present conditions (room temperature, vacuum, carbon surface) (Section 4).
8 Calculations (Section 1) show that the atomization energy required for Fe₂ is 2.2 eV (1.1
9 eV/atom), rising to 4.3 eV (1.4 eV/atom) for Fe₃. The observed extended lifetime of the
10 amorphous cluster of Fe atoms indicates its stability when the number of atoms is above 10, as
11 confirmed by the observation that clusters containing approximately 10 Fe atoms never
12 crystallize nor dissociate back to individual atoms (Supplementary Fig. 9 and 10). Significantly,
13 once the growth of the Fe cluster is completed, the Fe cluster containing 17 atoms stays
14 amorphous for over 142 seconds before crystallizing which we regard as evidence that a
15 metastable amorphous precursor cluster is necessary for the nucleation of γ -Fe. Under the present
16 experimental conditions, we also observe several examples of stable crystallites of larger sizes,
17 such as a γ -Fe crystallite with approximately 100 atoms (Supplementary Fig. 10). Overall, these
18 observations are consistent with the existence of two free-energy barriers and an amorphous
19 precursor state during the heterogeneous nucleation of γ -Fe which is consistent with the pathway
20 proceeding via a TSNM. While more than 10 Fe atoms appear to be necessary and 17 Fe atoms
21 appear to be sufficient to produce an ordered crystalline nucleus, it must be noted the critical
22 number of atoms may be different under conditions which differ from those in our experiments,
23 as e-beam irradiation has been shown to affect the nucleation process previously^{11,25}. Being

1 continuously irradiated by the e-beam, the γ -Fe crystallite begins to interact with the host SWNT
2 leading to removal of carbon atoms from the SWNT, propagating the growth of a vacancy
3 defect, which finally leads to the rupture of SWNT after 170 s (Section 8)²⁹.

4 **Au crystal nuclei formed from amorphous nanocluster.** The importance of initially forming a
5 metastable amorphous precursor is further illustrated by nucleation of Au crystallites (Fig. 4). At
6 the start of the experiment an initial stable amorphous Au cluster can be observed confined in the
7 SWNT. Some Au atoms diffuse into the adjacent carbon nanostructure (violet arrow in Fig. 4a).
8 In the first 16 seconds of e-beam irradiation the atomic structure of the cluster is extremely
9 dynamic and appears amorphous (Supplementary Video 2). At 17 s, a metastable crystallite with
10 a diameter of less than 1 nm can be observed in the Au cluster (red arrow, Fig. 4a), which is
11 confirmed by analysis of the corresponding FFT pattern (Fig. 4b). This tiny crystallite dissociates
12 in the following 5 seconds and reappears again at 23 s. When the diameter of the crystallite
13 reaches \sim 1 nm it becomes stable over extended periods of time with a well-ordered structure of
14 the (111) face of Au observed. From this point, the nucleation process gradually extends from
15 the tiny crystallite to the whole Au cluster in the following 348 seconds, reaching a final
16 crystallite size of \sim 2 nm long and \sim 1 nm wide at 370 s. The Au crystallite maintains its
17 orientation in the first 28 seconds of the nucleation process from 23 s to 51 s and subsequently
18 rotates or transforms, displaying different orientations from 51 s to 330 s. During the final stage
19 of nucleation from 331 s to 370 s, the Au crystallite rotates or transforms again to the original
20 (111) face, as can be seen in the FFT patterns of the areas marked with red frames (Fig. 4a,b). By
21 evaluating the intensity of the spots corresponding to crystalline gold in the FFT patterns, the
22 degree of crystallinity can be estimated (Fig. 4c) showing an abrupt increase of the atomic

1 ordering in the Au cluster during heterogeneous nucleation that demonstrates that crystallization
2 of Au has occurred from an amorphous precursor.

3 The maximum transferred kinetic energy ($E_{T,max}$) from the incident 80 keV electrons to
4 the Au atoms is 0.96 eV (Section 2, in which the corresponding differential cross section as well
5 as the total cross section of elastic scattering is included). Thus, when being irradiated by the e-
6 beam, the total free energy of the Au cluster increases allowing it to overcome the energy barrier
7 for transformation from amorphous to crystalline (Supplementary Fig. 5, Section 4). Previous
8 work has demonstrated that energy transferred from the electron beam can influence, melt and
9 even vaporize the different metal nanocrystals²⁸. In the case of Au, the metastable amorphous
10 cluster dynamically changes the atomic structure before finally crystallizing under the influence
11 of the electron beam (Fig. 4d). Therefore, we can conclude that the size of the amorphous Au
12 cluster is smaller than the critical size for crystallization under sample preparation conditions but
13 larger than the critical size for crystallization under the TEM observation conditions, i.e. only
14 under the influence of e-beam irradiation it has enough energy to overcome the energy barrier to
15 crystallization. It should be noted that our experiments reveal a discernible Au crystallite with a
16 radius of approximately 0.45 nm, which is much smaller than the crystal nucleus of 2 nm
17 observed for this metal in the aqueous solution of a liquid TEM cell¹¹ owing to the different
18 conditions for nucleation.

19 **Re crystal nuclei formed by coalescence.** Increases in the number of atoms in the cluster helps
20 to overcome the free energy barrier and promotes the nucleation process. Therefore, the
21 coalescence of clusters, typically ignored by the classical nucleation theory, can be an important
22 process for nucleation as it enables a rapid increase of the cluster size (Section 4). We observe
23 this effect by imaging coalescence of two stable amorphous Re clusters into a larger amorphous

1 metastable cluster that subsequently crystallizes into a Re crystallite. At the beginning of the
2 TEM time series, two pre-existing sub-nanometer amorphous Re clusters with approximately 10
3 atoms each are present in the host SWNT (Fig. 5). The left cluster is mobile, translating along the
4 cavity of the SWNT. The right cluster is fixed on the SWNT by metal-carbon bonding and partly
5 covered by a carbon shell, which can be regarded as the substrate for heterogeneous nucleation.
6 At 135 s, the left cluster translates and attaches to the carbon shell of the right cluster. They come
7 into contact briefly on two occasions via single Re atom at 151 s and 177 s, and then completely
8 coalesce in 3 seconds from 183 s to 185 s. The resultant cluster contains approximately 20 atoms
9 of Re which appears to be above the critical number allowing the metal to overcome the free
10 energy barrier for crystallization (Supplementary Fig. 6, Section 4). The process of
11 crystallization starts with the formation of a metastable amorphous state at 185 s, followed by
12 reorganization of Re atoms into a crystallite between 185 and 308 s, which is slightly faster than
13 the nucleation we observe in the case of γ -Fe. At 308 s, the Re crystallite with recognizable
14 crystalline structure is observed followed by 124 seconds of restructuring while maintaining the
15 crystallinity which can be clearly observed as distinguishable lattice planes in the ‘Ordered
16 Crystallite’ stage and quantified by FFT (Fig. 5b,c). The overall crystallite formation of Re
17 follows the same TSNM pathway as Au and Fe, with the only difference that the critical size (or
18 number of atoms) required for crystallization is achieved by coalescence of two amorphous Re
19 clusters.

20

21 **Conclusions**

22 We have imaged the heterogeneous nucleation of three different metals, γ -Fe, Au and Re in
23 SWNT, with atomic resolution. All three nucleation processes observed under electron beam

1 irradiation and at room temperature are consistent with a TSNM framework, proving the validity
2 of this theoretically postulated mechanism¹⁴. We have directly observed the existence of
3 metastable amorphous precursor and demonstrated its necessity for the crystallite nucleation
4 processes. The size and the number of atoms in the amorphous precursor are critically important
5 for the emergence of a crystallite, in the case of all three metals the critical size is in the sub-2
6 nm range, and the number of atoms necessary for successful crystallization of both γ -Fe and Re
7 lies between 10 and 20. The combined use of a SWNT as the substrate for heterogeneous
8 nucleation and channel for delivery of metal atoms, and the electron beam as a source of energy
9 to simultaneously drive the process and act as an imaging tool, sheds light on formation of
10 crystal nucleus at the sub-nanometer level – a challenging size range for any other analytical
11 methods. These results are particularly important for iron, gold and rhenium in the carbon-rich
12 environments present in a variety of industrial contexts, including Fischer-Tropsch catalysis,
13 growth of graphene by chemical vapor deposition or steel manufacturing.

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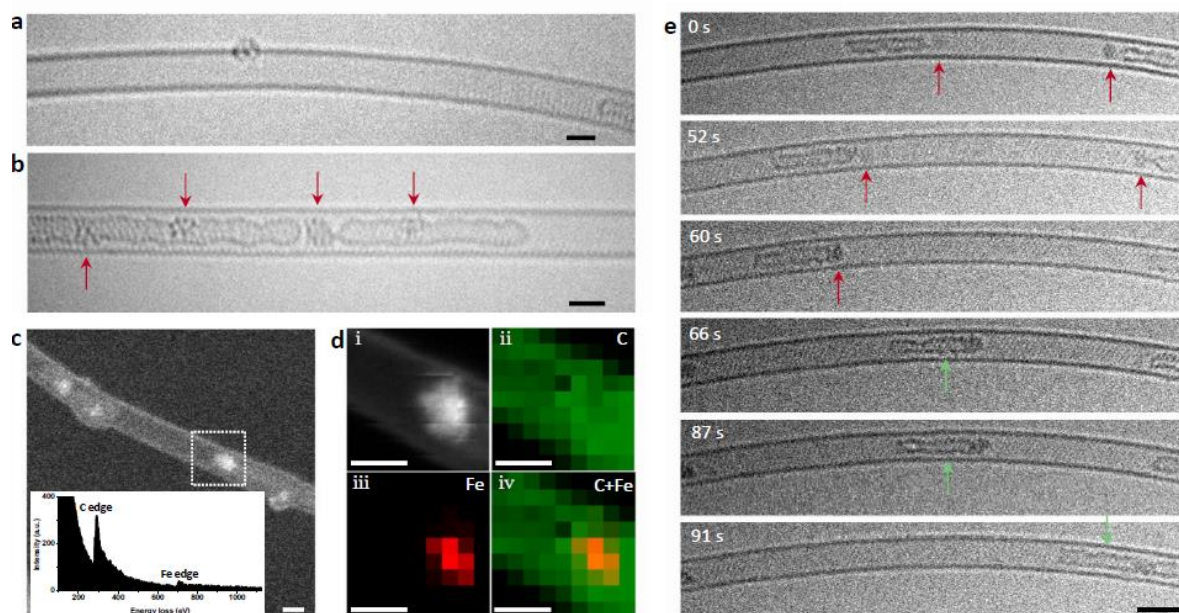
17
18 **Author Contributions** R. M. prepared the samples. C. S. carried out initial analysis of the
19 sample. T. W. C. developed the methodology of filling nanotubes with metal precursors. Z. L., J.
20 B. and K. S. performed the EELS mapping of the sample. K. C. and J. B. investigated of the
21 sample by AC-HRTEM and recorded the videos of nucleation. K. C., J. B., A. N. K. and U. K.
22 discussed the results and analyzed the data. E. B. and S. T. S. carried out theoretical modelling.

1 K. C. J. B., A. N. K. and U. K. drafted the manuscript. All the authors have revised the
2 manuscript. U. K. and A. N. K. supervised the research.

3

4 **Competing interests**

5 The authors declare no competing interests.



6

7 **Figure 1 | Structure of Fe@SWNT and time-series AC-HRTEM images of an ‘atomic**

8 **injector’.** **a**, AC-HRTEM image showing a SWNT with three Fe atoms on its wall; scale bar,

9 1 nm. **b**, A SWNT containing Fe clusters and amorphous carbon combined in a variety of

10 different structures (Fe clusters are indicated by the red arrows). The first, second and fourth Fe

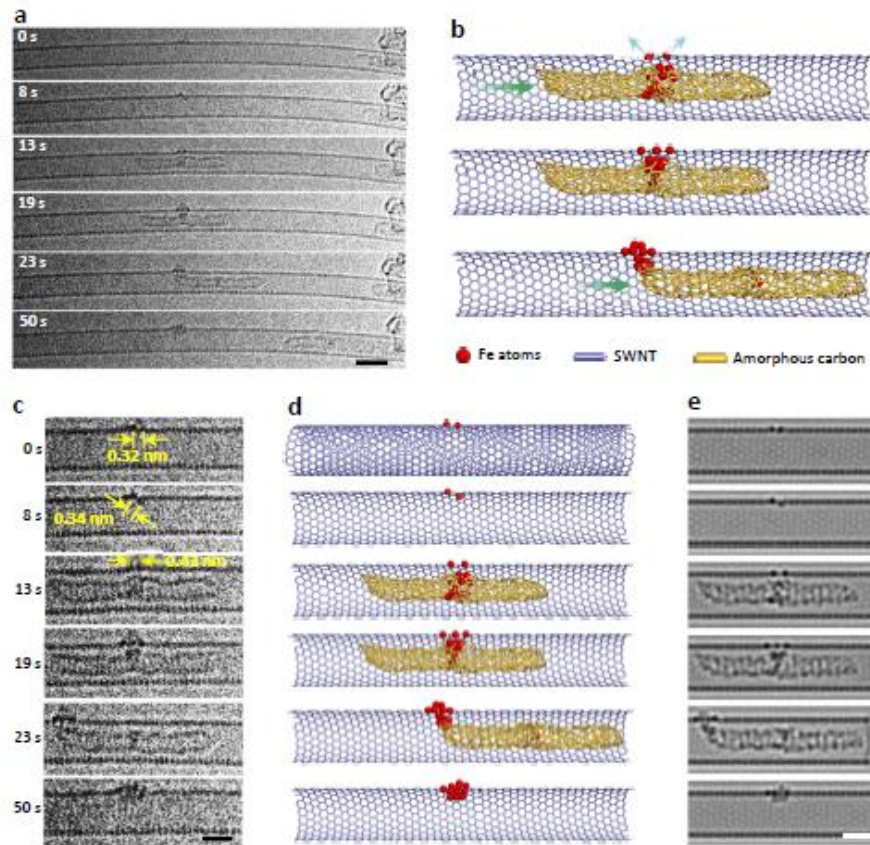
11 clusters from left to right combine with amorphous carbon while the third is an isolated Fe

12 cluster; scale bar, 1 nm. **c**, HAADF-STEM image of Fe@SWNT with EELS spectrum recorded

13 from the white box area (inset); scale bar, 1 nm. **d**, EELS mapping of the selected area in **c**. **i**,

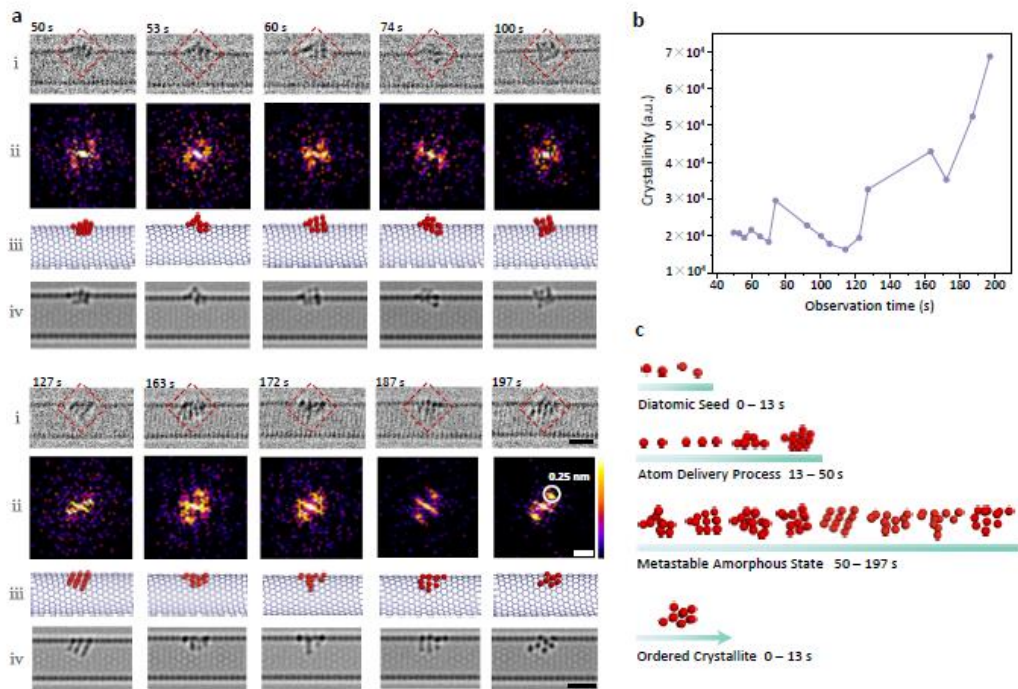
14 HAADF-STEM image of selected area; **ii**, distribution of carbon; **iii**, distribution of iron; **iv**,

1 distribution of carbon and iron; scale bars, 1 nm. **e**, A typical example of a Fe@SWNT based
 2 atomic injector. A time-series of AC-HRTEM images showing: a Fe cluster translating back and
 3 forth from 0 s to 60 s, and a Fe cluster-amorphous carbon complex translating from the left side
 4 to the right from 60 s to 91 s under 80 keV e-beam irradiation. The positions of the Fe cluster are
 5 tracked by red arrows, the positions of Fe cluster-amorphous carbon complex are tracked by
 6 green arrows; scale bar, 2 nm. More detailed information of this process is shown in
 7 Supplementary Fig. 2.



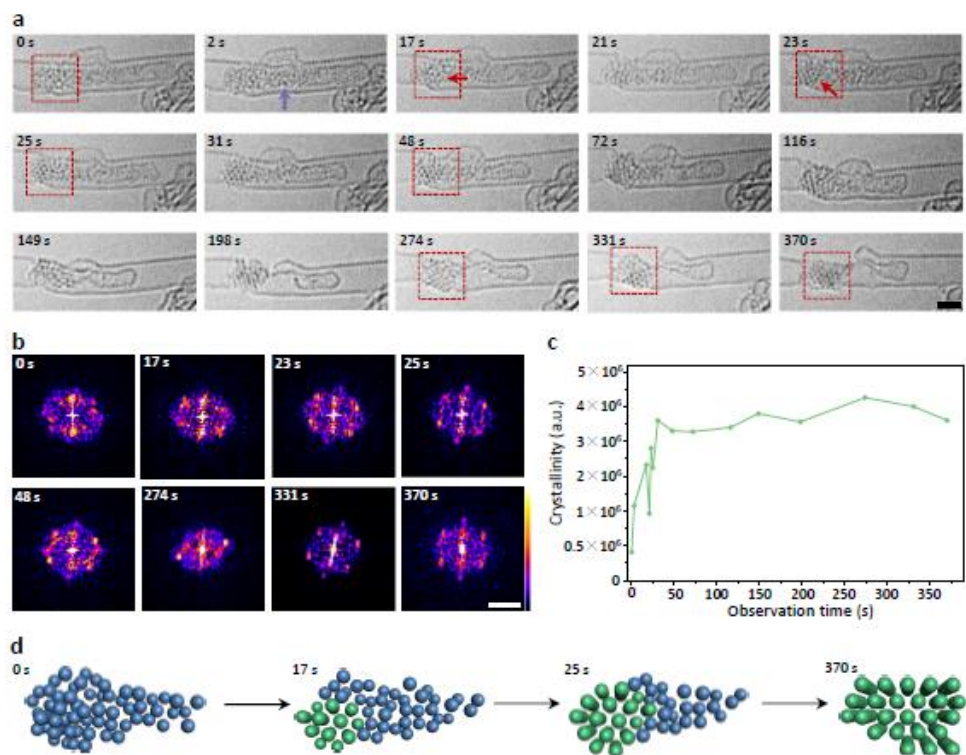
8
 9 **Figure 2 | Sequential AC-HRTEM images and corresponding simulations showing the first**
 10 **and second stages of γ -Fe crystallite nucleation. a**, AC-HRTEM raw images of the first stage
 11 from 0 s to 13 s, ‘Diatomic Seed’ formation, and the second stage from 13 s to 50 s, the ‘Atom

1 Delivery Process'. Exposure time, 0.25 s per frame; scale bar, 2 nm. **b**, Schematic showing the
 2 role of the atomic injector, in which the atomic injector is propelled to the seed providing
 3 individual Fe atoms, before it continues moving along the SWNT cavity (the blue arrows
 4 indicate the steric hindrance between the diatomic seed and the atomic injector and the green
 5 arrows indicate the direction in which the atomic injector moves). **c**, Enlarged regions of the AC-
 6 HRTEM series shown in **a** with atomic separations shown. The fifth row in **c** and **e** are shifted to
 7 enable full view of the atomic injector. The distances between two Fe atoms in the first three
 8 frames are labelled in yellow; scale bar, 1 nm. **d**, Modeled structures corresponding to the
 9 experimental images in **c**. The chiral index of the SWNT is $n = 18, m = 2$ as calculated in
 10 Supplementary Fig. 14. **e**, Simulated TEM images from the structures in **d**. The SWNT in the
 11 modeled structures in **b** and **d** have clipping planes to highlight the structure of Fe clusters; scale
 12 bar, 1 nm.



13

1 **Figure 3 | Sequential AC-HRTEM image and corresponding image simulations showing**
2 **the third and fourth stages of γ -Fe crystallite nucleation. a,** Time-series AC-HRTEM images
3 of the third ‘Metastable Amorphous State’ stage from 50 s to 187 s, and the fourth ‘Ordered
4 Crystallite’ stage at 197 s are listed in the first row (i); scale bar, 1 nm. The exposure time for the
5 frames between 50 s and 127 s is 0.5 second, and 1.0 second from 127 s to 197 s. The FFT
6 corresponding to the outlined area of AC-HRTEM images are depicted in the second row (ii) and
7 used to quantify the crystallinity of the Fe cluster at each point in time (via the appearance of an
8 extra Fe-reflection, Section 6); scale bar, 5 1/nm. The modeled structures and simulated TEM
9 images for the proposed structures of the Fe clusters which correspond to the AC-HRTEM
10 images in the same column are presented in the third (iii) and fourth rows (iv); scale bar, 1 nm. **b,**
11 Quantified measure of the crystallinity by comparing the intensities of the reflection spots in the
12 FFT of the Fe clusters. The measured reflection spots are chosen from the probable characteristic
13 diffraction spot areas where the γ -Fe-reflection appears. **c,** Timeline of the whole experiment
14 with the structural evolution of the γ -Fe crystallite consisting of the 4 stages of crystallite
15 formation.



1

2 **Figure 4 | E-beam stimulated nucleation of Au crystallite from the amorphous state. a,**

3 Time-series AC-HRTEM images showing an amorphous Au cluster gradually transforming into

4 its crystalline structure under 80 keV e-beam irradiation. The formed crystallite is indicated by

5 red arrows; scale bar, 1 nm. **b,** FFT patterns of the corresponding areas framed by red dotted

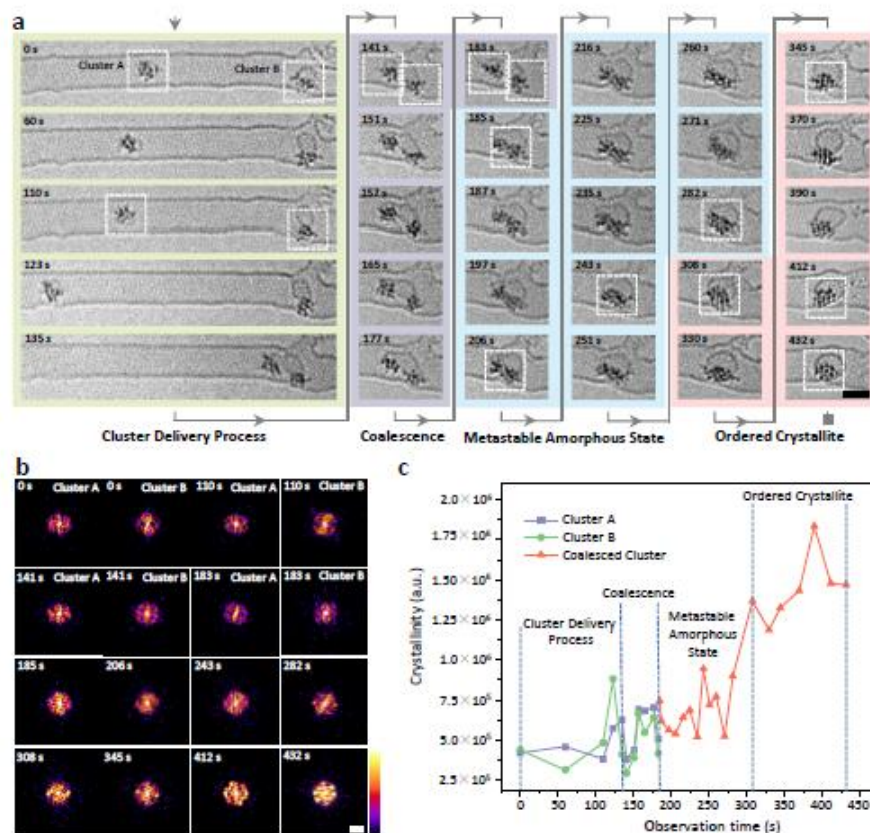
6 boxes in **a** demonstrating the formation of the Au crystallite. Some Au atoms in this Au cluster

7 diffuse into the neighboring carbon nanostructure as indicated by the violet arrow; scale bar,

8 1/5 nm. **c,** Quantified crystallinity of the Au cluster during the nucleation in **a** and **b.** **d,**

9 Schematics of the gradual nucleation of the Au crystallite (the amorphous parts are shown in

10 blue, the crystalline parts in green).



1

2 **Figure 5 | E-beam stimulated nucleation of a Re crystallite by coalescing two amorphous**

3 **sub-nano Re clusters. a**, Time-series AC-HRTEM images showing the four key stages of Re

4 crystallite nucleation starting with two amorphous sub-nm Re clusters (Supplementary Video 3).

5 From 0 s to 135 s, one amorphous cluster located at the left of the SWNT translates and attaches

6 to another amorphous cluster located at the right of the SWNT, which is the first stage of Re

7 nucleation, ‘Cluster Delivery Process’. From 141 s to 183 s, the two clusters contact each other

8 and then coalesce into one amorphous cluster, which is the second stage: ‘Coalescence’. The

9 coalesced amorphous cluster ceaselessly changes its structure from 185 s to 282 s, ‘Metastable

10 Amorphous State’ stage. At 308 s, a crystallite is formed and keeps on restructuring for a further

11 124 seconds, ‘Ordered Crystallite’ stage; scale bar, 1 nm. **b**, FFT patterns of the corresponding

12 areas framed by white dotted boxes in **a** analyzing the periodic structural information of Re

1 cluster and crystallite; scale bar, 5 $\frac{1}{\text{nm}}$. **c**, Quantification of the degree of crystallization for the
2 Re clusters at the different stages depicted in **a**. Cluster A and Cluster B are the small Re clusters
3 on the left and the right sides of the image at the beginning of the experimental image series,
4 respectively.

5

6 **Methods**

7 **Materials.** Arc-discharge SWNTs were annealed in air to open their termini. The organometallic
8 complexes $\text{Fe}(\text{C}_5\text{H}_5)_2$, $\text{Au}(\text{CO})\text{Cl}$ and $\text{Re}_2(\text{CO})_{10}$, were respectively sealed under vacuum in a
9 quartz ampoule and heated at a temperature slightly above the vaporisation point of ferrocene
10 ($300\text{ }^\circ\text{C}$), $\text{Au}(\text{CO})\text{Cl}$ ($125\text{ }^\circ\text{C}$) and $\text{Re}_2(\text{CO})_{10}$ ($150\text{ }^\circ\text{C}$) for 3 days to ensure complete penetration
11 of the SWNT by the ferrocene, $\text{Au}(\text{CO})\text{Cl}$ and $\text{Re}_2(\text{CO})_{10}$ vapors. The samples were then rapidly
12 cooled to room temperature and the SWNTs washed with tetrahydrofuran (100 mL) to remove
13 any species from the outside of the SWNTs. Then the samples were heated at $500\text{ }^\circ\text{C}$ for 3 h
14 under argon in a pyrex tube to remove the ligands.

15 **TEM imaging and simulations.** The materials were dispersed in methanol and drop-cast onto
16 lacey carbon-coated copper TEM grids. Time-series AC-HRTEM images in Supplementary
17 Video S1-3 were carried out on an image side C_s -corrected FEI Titan 80-300 TEM operated at
18 80 kV at room temperature. The TEM specimen was heated in air at $150\text{ }^\circ\text{C}$ for 5 min shortly
19 before insertion into the TEM column. The HAADF-STEM imaging and corresponding EELS
20 spectrum in Fig. 1 were performed on a JEOL 2100F with a cold field-emission gun and an
21 aberration DELTA-corrector for the illumination system operated at 60 kV. TEM image
22 simulation was carried out using the multislice program QSTEM. Note, γ -Fe was observed to
23 have kept its crystalline structure after it formed during the experiment (197 sec to 336 sec) but

1 the related images were not acquired because we did not realize the importance of this
2 observation until the cutting process started.

3

4 **Data availability**

5 All data supporting the findings of this study are available in the manuscript or the
6 Supplementary Information. The data of ‘electron elastic scattering cross section’ that support
7 the findings of this study are publicly available online at [https://www.nist.gov/publications/nist-](https://www.nist.gov/publications/nist-electron-elastic-scattering-cross-section-database-version-40)
8 [electron-elastic-scattering-cross-section-database-version-40](https://www.nist.gov/publications/nist-electron-elastic-scattering-cross-section-database-version-40).

9