Plumbing carbon nanotubes

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Since their discovery, the possibility of connecting carbon nanotubes together like water pipes has been an intriguing prospect for these hollow nanostructures. The serial joining of carbon nanotubes in a controlled manner offers a promising approach for the bottom-up engineering of nanotube structures—from simply increasing their aspect ratio to making integrated carbon nanotube devices. To date, however, there have been few reports of the joining of two different carbon nanotubes[1–3]. Here we demonstrate that a Joule heating process, and associated electro-migration effects, can be used to connect two carbon nanotubes that have the same (or similar) diameters. More generally, with the assistance of a tungsten metal particle, this technique can be used to seamlessly join any two carbon nanotubes—regardless of their diameters—to form new nanotube structures.

In this study, carbon nanotubes (CNTs) were manipulated inside a transmission electron microscope (TEM) with a dedicated specimen holder. A piezo-driven stage enabled three-dimensional movement with a precision better than 0.5 nm, using a tungsten tip to manipulate individual CNTs while under TEM observation. A voltage could be applied to the CNTs and the current through them was measured. Three different geometries were considered for the joining of CNTs, as shown in the schematic model in Fig. 1.

Joining of two single-walled CNTs (SWNTs) having identical or similar diameters was attempted first. For this purpose, two CNTs arising from the same tube were created using an electrical breakdown process. When an individual SWNT bridges a gap between a W-tip and a counterpart electrode (a palladium wire), a high current can be introduced through the SWNT by applying a voltage between the tip and electrode, causing the diameter midway along the length of the SWNT to become gradually narrower (Fig. 2a). When the current reaches ~12 μA, the SWNT is split into two parts at the narrowed section, each part having a closed end or cap (Fig. 2b). The two capped SWNTs may be mechanically re-contacted in a 'cap-to-cap' geometry by moving the one mounted on the W-tip such that it approaches the other (Fig. 2c). The voltage and current are then gradually raised from zero. On reaching threshold values of 1.6 V and ~6 μA (corresponding to a current density of $\sim 7 \times 10^8$ A cm^{-2}), the two SWNTs suddenly join again into a CNT having its own unique geometry (Fig. 2d; see also Supplementary Information, Movie S1). No intermediate process has yet been observed in this joining stage, as it occurs quickly (within 0.5 s, which is less than the typical recording time). The diameter change is quite smooth across the junction, and no residual node is found in the newly formed SWNT. Some new local protrusions appear on the joined SWNT (see arrowheads in Fig. 2d).

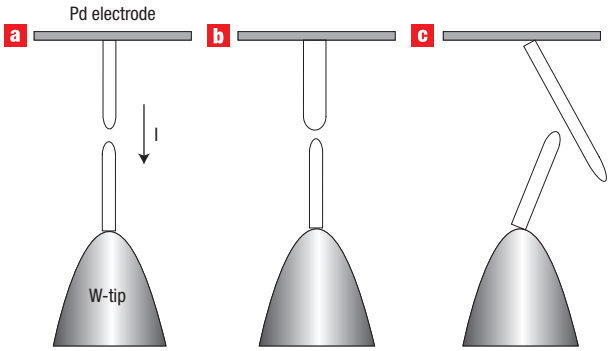

Figure 1 Schematic images of three typical geometries for joining CNTs. **a**, 'Cap-to-cap' joining of two CNTs with the same or similar diameter. **b**, 'Cap-to-cap' joining of two CNTs with different diameters. **c**, 'Cap-to-wall' joining of two CNTs to form a Y- or T-type junction. A voltage is applied between the three-dimensional mobile W-tip and the Pd electrode, thus introducing a current through the CNTs.

The whole process, including breaking and joining, could be repeated many times on the same SWNT (up to seven times so far in our experience; see Supplementary Information, example 13 in Table S1), and the threshold voltage and current are well reproduced during the cycles. No obvious dependence on the polarity of input voltage was found during our experiments. (See Supplementary Information, Fig. S1, for another example of joining two double-walled nanotubes, DWNTs.)

Joining CNTs having different diameters has also been attempted. A typical process among numerous attempts is shown in Fig. 2e–g, where two SWNTs of different diameters (2.9 nm for the upper one and 1.5 nm for the lower one) are contacted in a 'cap-to-cap' geometry. An obvious deformation appears on the cap of the larger SWNT (see arrowhead in Fig. 2f) when the current reaches ~10 μA with a bias voltage of 1.9 V. If the bias voltage is increased further, the two SWNTs quickly detach and separate from each other. Their cap structures apparently change during this process, and as a result both SWNTs undergo shrinkage in their length—a decrease of ~0.3 nm for the upper one and ~0.6 nm for the lower one (Fig. 2g; see also Supplementary Information, Movie S3). Such behaviour has been attributed to plastic deformation associated with the carbon evaporation of CNTs (refs 4, 5). Further additional joining attempts were attempted by re-contacting the two SWNTs, but

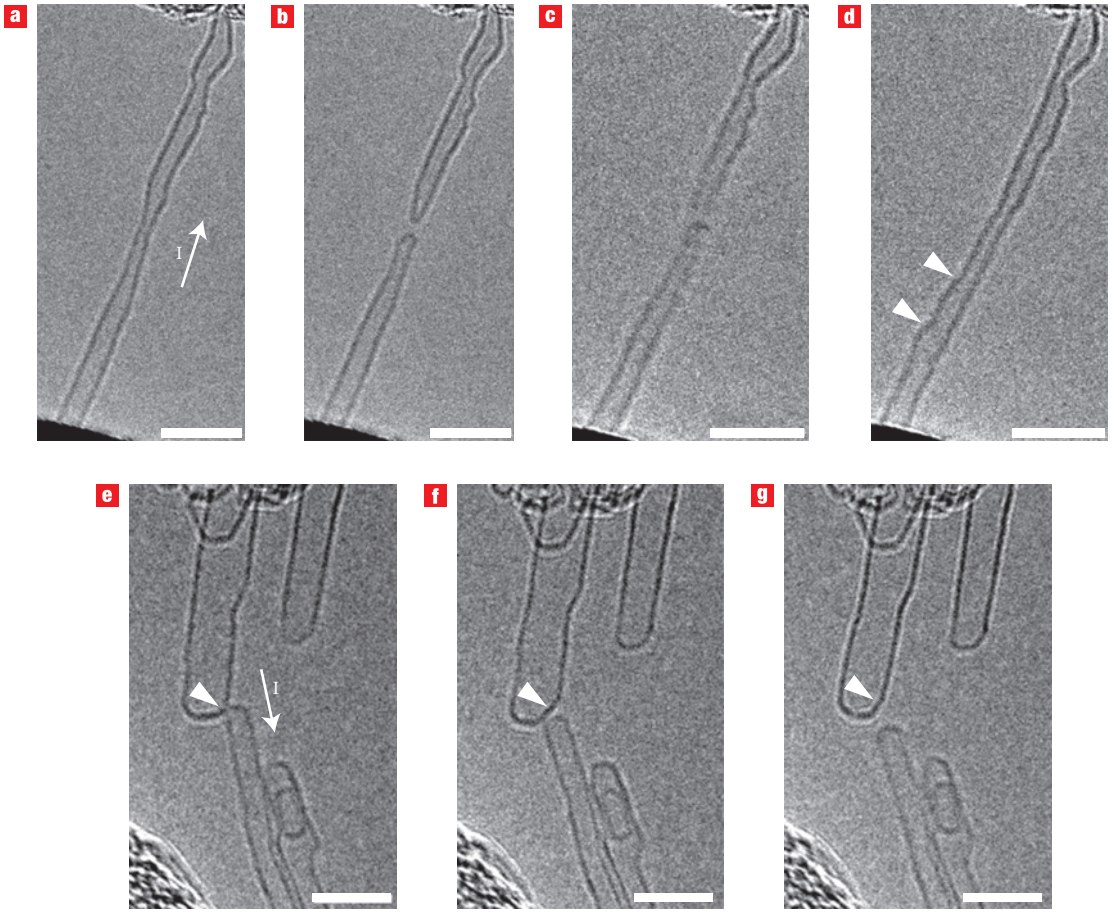

Figure 2 Successful and unsuccessful joining attempts on two different types of SWNTs. a–d, Successful joining of an SWNT split into two separate SWNTs by applying a large voltage (**a**,**b**), where the arrow in **a** indicates the direction of the current. The two SWNTs re-contact each other (**c**) and a new SWNT forms (**d**), showing some local protrusions appearing (arrowheads). **e–g**, Unsuccessful joining attempt using two SWNTs of different diameters (**e**). The arrow in **e** indicates the direction of the electric current. An obvious deformation appears on the cap of the upper SWNT (**f**, arrowhead). The two SWNTs detach from each other very quickly (**g**). Scale bars are 5 nm in all panels.

Table 1 Statistical data for joining attempts of various types of CNTs.

Types of CNTs	Joining geometry	Number of attempts	Number of successful joining	Description of failure
Same diameter and origin	Cap-to-cap	13	13	–
	Cap-to-wall	4	0	Shrinkage
Different origins and diameters	Cap-to-cap	16	0	Shrinkage
	Cap-to-wall	4	1	Shrinkage

with no success. Instead, they would always detach and shrink in length, even with a sub-threshold input voltage and current applied for as long as 10 min (see Supplementary Information, Movie S4).

By simply applying a voltage and introducing a current, two CNTs with the same or similar diameter can indeed be joined, but it seems to be intrinsically difficult to join two CNTs with completely different diameters. In order to exclude any exceptional events, a systematic investigation of the joining of a large number of CNTs was performed. Table 1 presents data for 37 examples of various types of CNTs chosen for joining (see Supplementary Information, Table S1, for details of these experiments). In the case of 'cap-to-cap' joining, all 13 attempts were successful when the CNTs stemmed from the same tube, without exception, but all 16 specimens failed to join when CNTs with different diameters were randomly chosen. Attempts to form a Y-type junction in the 'cap-to-wall' geometry failed in 7 of 8 attempts (see Supplementary Information, Fig. S2, for the one exception).

Two CNTs made from the electrical breakdown of a single nanotube are likely to have the same chirality, but two CNTs having different diameters should have different chiralities. The data in Table 1 may therefore give an important indication for a strict diameter and/or chirality selection rule, as proposed for the 'wall-to-wall' coalescence of SWNTs (refs 1, 6). The existence of some topological defects, such as a pentagon–heptagon pair, can induce a chirality change across a junction[7,8], thus there must be a tolerance level for chirality matching when joining two CNTs.

The seamless joining of two CNTs requires the rearrangement of the carbon networks. In particular, a closed cap contains a number of pentagons that should be activated to accommodate the shape change. According to theoretical simulations for the

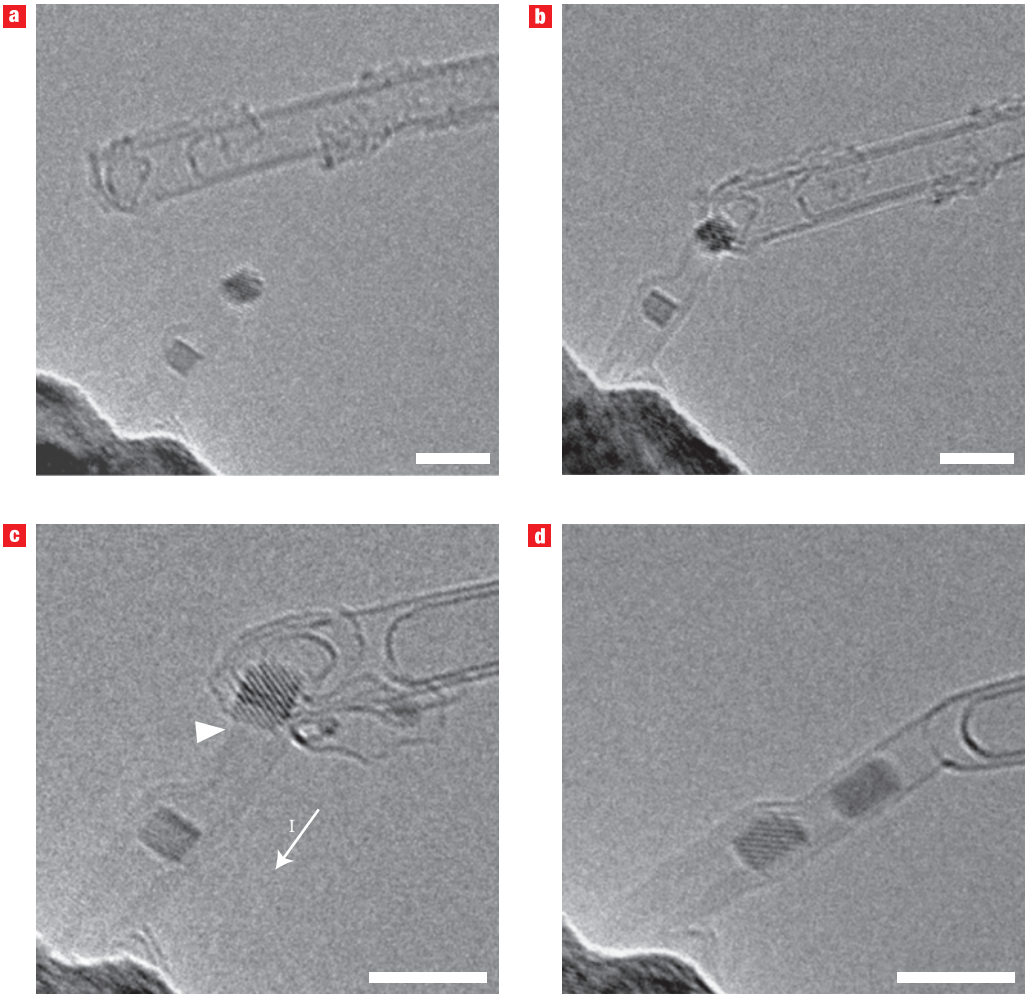

Figure 3 W-assisted joining of two DWNTs. a, The two separate DWNTs have different diameters. **b**, The DWNTs contact each other. **c**, The W particle is controlled to migrate towards the larger DWNT (upper) under a current ~25 μA, then the outer shell of the smaller DWNT starts to join with the graphitic layer outside the cap of the larger DWNT (indicated by the arrowhead). **d**, A seamless connection is formed between the two DWNTs after annealing and moving the W particle back and forth. The scale bars are 5 nm in all panels.

fusion of fullerene cages and CNTs (refs 9–11), a sequence of Stone–Wales (SW) transformations[12] is responsible for the joining. The SW transformation involves a C–C bond flip and leads to mobile topological defects. A typical CNT joining process requires several tens of SW steps. Each of the SW transformations should occur in the range of femto- or nano-seconds. It is therefore reasonable that no intermediate stage during the joining was observed in these experiments, because this is far beyond the time resolution of our image-recording device. The required threshold value for the applied voltage and current should correspond to the activation energy for the SW transformations and their migrations, which are estimated theoretically as a few eVs (refs 9–11).

One contribution for the required activation energy should come from Joule heating. Previous experiments on the coalescence of C_{60} required a high temperature, ranging from ~1,100 K to ~1,500 K, and over 10 h reaction time[13]. 'Wall-to-wall' and 'cap-to-wall' coalescences of CNTs were realized at a temperature of 1,100 K and with irradiation from ultra-high energetic electrons of 1.25 MeV (refs 1, 2, 6). By adopting the proposed thermal conductivity of ref. 14, a rough estimation gives a temperature range for our experiments of ~600–1,200 K. Here we assume that the irradiation of 120 keV electrons does not have a massive contribution to the joining process, because the joining conditions did not change when we blocked the incident electron beam. Joule heating alone is not sufficient for the generation and migration of topological defects; therefore, there must be some other contributions involved such as the electro-migration mechanism[15]. As the current density usually reaches between about 1×10^7 A cm^{-2} and 1×10^9 A cm^{-2}, this value could be extremely high at some thinner areas of the CNT, for example at the contact point of the cap apex. For such a high current density, the electro-migration process becomes particularly important and should not be negligible. The direct momentum transfer from the carriers to the lattices, associated with a high electric field, will cause the local carbon atoms to strongly interact, which could assist in the joining process and/or in the shrinkage process (through carbon evaporation).

Local protrusions with positive curvature appear after joining both SWNTs and DWNTs, implying the existence of pentagons. They may originate from the caps of the CNTs (a closed cap needs a number of pentagons), and then should be driven away

from the junction to conform to the topological rule (uniform connections do not need many pentagons), followed by their migration along the tube[16].

The total energy barriers required for the generation of a pentagon–heptagon pair and their migration along the carbon network through sequential SW steps may be higher than that of evaporation of a carbon dimer from the caps of the tubes. In the case of two CNTs with a mismatch in their diameters, length shrinkage, dominated by the evaporation of carbon atoms, occurs before the pentagon–heptagon pairs are created and mobilized. This is one of the possible reasons why joining fails for CNTs having different diameters. In order to overcome this drawback, we have inserted W particles to create a joint with two CNTs of completely different diameters by intentionally reducing the energy barrier of SW defect migrations and/or catalysing the graphene network re-arrangement.

Sequential TEM images illustrate the process of W-assisted joining of two DWNTs with different diameters (Fig. 3). The upper DWNT in the panels has an outer-diameter of 3.2 nm, and the lower one a diameter 2.0 nm near the cap. Two W particles are encapsulated inside the smaller DWNT: one is at the cap and the other in the middle around a kink (Fig. 3a; see also Methods for a description of *in situ* W insertion). As shown in Fig. 3b, once the two caps are in contact, the W particle near the cap of the smaller DWNT moves towards the other DWNT under a high current flux. The direction of its movement could be controlled by the polarity of the applied voltage. (Such an electro-migration induced process has already been used for mass transfer through CNTs; refs 17, 18.) The two tubes then begin to share a graphitic layer (see arrowhead in Fig. 3c). Such an extra graphene layer should have been created through the W particle from the surrounding carbon atoms (see Supplementary Information, Movie S5). Annealing under a higher current and moving the W particle back and forth (by changing the polarity of the input voltage) has further improved the quality of the junction. Finally, a new CNT is fabricated and a seamless connection between the two DWNTs having completely different diameters has been successfully achieved (Fig. 3d). (See Supplementary Information, Movies S6 and S7, for more examples, and Table S2 for a summary of all 58 attempts.)

We would like to clarify two important points that can be deduced from the experiments shown in Fig. 3 and Movie S5 (see Supplementary Information). First, both the ordered lattice fringes and the regular crystalline shape demonstrate that the W particle remains in the solid state during the whole process, although its shape often changes instantaneously (the so-called 'quasi solid state')[19]. Second, the graphite shells can continuously dissolve into the W particle during migration under high current flux. Lattice fringes consistent with tungsten carbide are often observed in the particles.

The mechanism for the W-assisted joining of CNTs with different diameters should have some similarities with that for the W-catalysed growth of CNTs (ref. 20). During the migration of a W particle from one DWNT to another, a certain number of carbon atoms can dissolve into the W particle. The graphitic shells of the two DWNTs further grow owing to surface[21] or bulk diffusion[22] of the carbon atoms through the W particle.

We can now compare the differences in the joining mechanism with and without the W particles (see Supplementary Information, Fig. S3). The CNTs joining without W particles should require a relatively higher temperature in order to activate the topological defects, resulting in massive morphological changes in the CNT bodies (such as the newly formed protrusions seen in Fig. 2d and Fig. S1). However, in the experiments involving W particles, structural change arises only near the particles, and no massive morphological changes are observed in the CNT bodies. This fact implies that the joining with the W particle occurs at a considerably lower temperature, and also suggests that the energy barrier for the re-organization of graphene networks should have been significantly decreased. As well as W, other metals well-known as a catalysts for carbon graphitization, such as nickel or iron, should have a similar effect. Doped boron atoms have also been reported as a welder for the connection of CNTs (ref. 23).

This simple method, demonstrating the plumbing of CNTs like water pipes, will allow longer and multi-branched CNTs with serial junctions to be made by repeated joining, and may have uses for different applications. The results shown here have positive implications for device applications of CNTs such as field-effect transistors or current lead-wires. If they break down during operation, the nanotubes could be mended by application of a continuous inducing current.

METHODS

Our experiments were performed on a dedicated piezo-driven specimen holder (Nanofactory AB) inside a TEM (JEOL 2010F) operated at 120 kV. Commercially available SWNTs and MWNTs were used. As-grown CNTs were directly assembled onto the surface of a clean Pd electrode, and then transferred and fixed onto the immobile side of the specimen holder. Under TEM observation, individual CNTs extending from the edge of the Pd electrode or CNT bundles were often found. An electrochemically etched W-tip was mounted on the three-dimensional mobile side of the specimen holder, enabling manipulation of particular CNTs with a precision better than 0.5 nm. Simultaneously, we were able to apply a voltage between the W-tip and the Pd electrode, and introduce a current through the object CNTs. Sequential TEM images were recorded using a charge-coupled-device camera (Gatan 894) with a 0.5-s exposure time for each frame. The typical electron beam intensity used for observation and image recording was $\sim$18 A cm^{-2}. W particles could be inserted into the CNTs through a field emission initiated vacuum arc process[24] inside the TEM in the following manner. First, an individual CNT or bundles of CNTs were assembled onto the top of the W-tip through the electrical breakdown process, then the W-tip with CNTs was used as a field emitter by applying a large positive bias on the Pd electrode wire, with the W-tip grounded. A vacuum arc process occurred when the electric field reached several volts per nanometre or higher, part of the melting W being encapsulated into some CNTs. The insertion process has some similarities to that for the synthesis of metal-encapsulated CNTs (ref. 25).

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References

1. Terrones, M., Terrones, H., Banhart, F., Charlier, J.-C. & Ajayan, P. M. Coalescence of single-walled carbon nanotubes. *Science* **288,** 1226–1229 (2000).
2. Terrones, M. *et al.* Molecular junctions by joining single-walled carbon nanotubes. *Phys. Rev. Lett.* **89,** 075505 (2002).
3. Wang, M. S., Wang, J. Y., Chen, Q. & Peng, L. M. Fabrication and electrical and mechanical properties of carbon nanotube interconnections. *Adv. Funct. Mater.* **15,** 1825–1831 (2005).
4. Huang, J. Y. *et al.* Superplastic carbon nanotubes. *Nature* **439,** 281 (2006).
5. Ding, F., Jiao, K., Lin, Y. & Yakobson, B. I. How evaporating carbon nanotubes retain their perfection? *Nano Lett.* **7,** 681–684 (2007).
6. Yoo, M. *et al.* Zipper mechanism of nanotube fusion: theory and experiment. *Phys. Rev. Lett.* **92,** 075504 (2004).
7. Dunlap, B. I. Relating carbon tubules. *Phys. Rev. B* **49,** 5643–5650 (1994).
8. Hashimoto, A., Suenaga, K., Golter, A., Urita, K. & Iijima, S. Direct evidence for atomic defects in graphene layers. *Nature* **430,** 870–873 (2004).
9. Zhao, Y. F., Yakobson, B. I. & Smalley, R. E. Dynamic topology of fullerene coalescence. *Phys. Rev. Lett.* **88,** 185501 (2002).
10. Zhao, Y. F., Smalley, R. E. & Yakobson, B. I. Coalescence of fullerene cages: topology, energetics, and molecular dynamics simulation. *Phys. Rev. B* **66,** 195409 (2002).
11. Han, S. *et al.* Microscopic mechanism of fullerene fusion. *Phys. Rev. B* **70,** 113402 (2004).
12. Stone, A. J. & Wales, D. J. Theoretical studies of icosahedral C_{60} and some related species. *Chem. Phys. Lett.* **128,** 501–503 (1986).
13. Bandow, S., Takizawa, M., Hirahara, K., Yudasaka, M. & Iijima, S. Raman scattering study of double-wall carbon nanotubes derived from the chains of fullerenes in single-wall carbon nanotubes. *Chem. Phys. Lett.* **337,** 48–54 (2001).
14. Pop, E., Mann, D., Wang, Q., Goodson, K. & Dai, H. Thermal conductance of an individual single-wall carbon nanotube above room temperature. *Nano Lett.* **6,** 96–100 (2006).
15. Sorbello, R. S. Theory of electromigration. *Solid State Phys.* **51,** 159–231, (1998).
16. Suenaga, K. *et al.* Imaging active topological defects in carbon nanotubes. *Nature Nanotech.* **2,** 358–360 (2007).

17. Regan, B. C., Aloni, S., Ritchie, R. O., Dahmen, U. & Zettl, A. Carbon nanotubes as nanoscale mass conveyors. *Nature* **428,** 924–927 (2004).
18. Svensson, K., Olin, H. & Olsson, E. Nanopipettes for metal transport. *Phys. Rev. Lett.* **93,** 145901 (2004).
19. Iijima, S. & Ichihashi, T. Structural instability of ultrafine particles of metals. *Phys. Rev. Lett.* **56,** 616–619 (1986).
20. Kiang, C. H., Goddard III, W. A., Beyers, R., Salem, J. R. & Bethune, D. S. Catalytic effects of heavy metals on the growth of carbon nanotubes and nanoparticles. *J. Phys. Chem. Solids* **57,** 35–39 (1996).
21. Raty, J.-Y., Gygi, F. & Galli, G. Growth of carbon nanotubes on metal nanoparticles: a microscopic mechanism from ab initio molecular dynamics simulations. *Phys. Rev. Lett.* **95,** 096103 (2005).
22. Rodriguez-Manzo, J. A. *et al*. In situ nucleation of carbon nanotubes by the injection of carbon atoms into metal particles. *Nature Nanotech.* **2,** 307–311 (2007).
23. Endo, M. *et al*. Atomic nanotube welders: boron interstitials triggering connections in double-walled carbon nanotubes. *Nano Lett.* **5,** 1099–1105 (2005).
24. Dyke, W. P. & Trolan, J. K. Field emission: large current densities, space charge, and the vacuum arc. *Phys. Rev.* **89,** 799–808 (1953).
25. Ajayan, P. M. *et al*. Growth of manganese filled carbon nanofibers in the vapor phase. *Phys. Rev. Lett.* **72,** 1722–1725 (1994).

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Author contributions

C. J., K.S. and S.I. conceived and designed the experiments. C.J. performed the experiments and analysed the data. C.J. and K.S. co-wrote the paper. All authors discussed the results and commented on the manuscript.