Supplementary Information

Defect-induced junctions between single- or double-wall carbon nanotubes and metal crystals

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1. Tailoring metal-CNT junctions by an electron beam

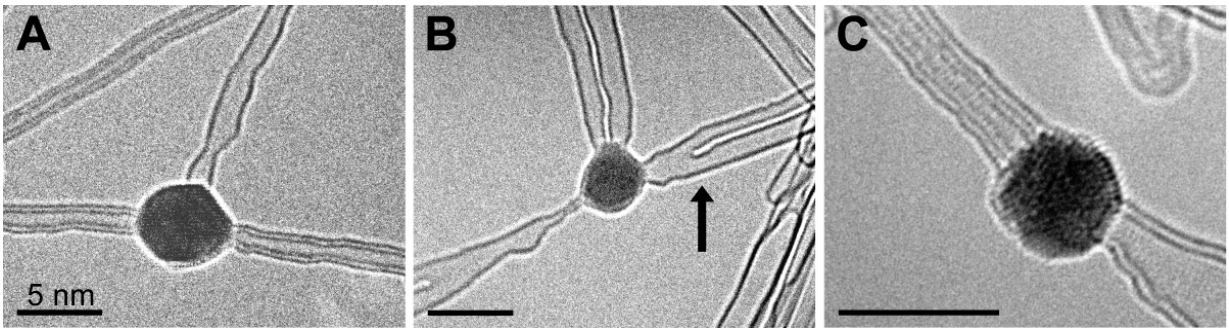

Figure S1: If more than one CNT is connected to a metal nanoparticle, further modifications can be induced by cutting specific nanotubes with the electron beam in order to produce structures of higher complexity, such as multi-branched junctions. The figure shows three examples of such structures, where different metals (Co, Fe, and Pt) work as “welding” agents between different nanotubes. (A) A DWNT and a SWNT were joined with a Co nanoparticle; afterwards, a SWNT branch was cut to form a T-type structure. The sample was held at 580°C. (B) Two SWNTs were connected with two other perpendicular SWNTs and a Fe nanoparticle at the node. In this case, after cutting of the lower branch, coalescence of the horizontal SWNTs was observed at the junction, following a “zipper” mechanism as indicated by the arrow. The sample was held at 680°C. (C) After joining a TWNT and a DWNT with a Pt particle, two branches were cut to form a continuous TWNT-Pt-DWNT structure. The sample was held at 480°C.

2. Atomistic simulations

We employed the spin-polarized density functional theory (DFT) as implemented in the plane-wave-basis-set VASP code.[1] We used projector augmented wave (PAW) potentials[2] to describe the core electrons and the generalized gradient approximation of Perdew, Burke, and Ernzernhof (PBE)[3] for exchange and correlation. A kinetic energy cutoff of 350 eV was used in most simulations. Test calculations with a cutoff of 400 eV showed that the binding energy has converged within at least 0.1 eV. We considered finite systems with a vacuum region around the tube and the particle. The studied model system consisted of a (7,0) SWNT and metal clusters composed of 55, 92, and 116 atoms. As the ultimate case, we also studied the bonding of a (8,0) SWNT to the (111) Fe surface.

As the metal particles observed in our experiments were considerably larger than those used in our DFT calculations, we also employed an analytical many-body potential[4] to study Fe-C systems composed of about 10^3 atoms and matching the experimental system sizes. To find the minimum energy configuration within the analytical potential (AP) approach, we first annealed the structure at 400ºC for 30 ps, then quenched the system to 0K. In DFT simulations the two parts of the system were put within the interaction range, then the geometry was fully optimized.

To estimate how much energy can be released when the metal particle is adsorbed on a pristine SWNT (tube stem), we calculated the adsorption energy for the configuration shown in Fig. S2. It is known that graphene binds weakly to metals (binding energy per atom is in the range of 0.05-0.2 eV[5]) through weak covalent and van der Waals-type bonds. The interaction energy proved to be slightly higher in our DFT simulations (about 0.4 eV/atom), possibly due to a higher reactivity of small metal particles associated with under-coordinated atoms at the verges of the particle as compared to low-index surfaces. AP simulations for bigger systems gave small binding energies of less than 0.05 eV per C atom, or no binding at all, depending on the geometry/orientation. As the binding energy of a metal particle to the “stem” of the nanotube is much smaller than the energy due to carbon-metal covalent bonds, we did not take the adsorption energy into account.

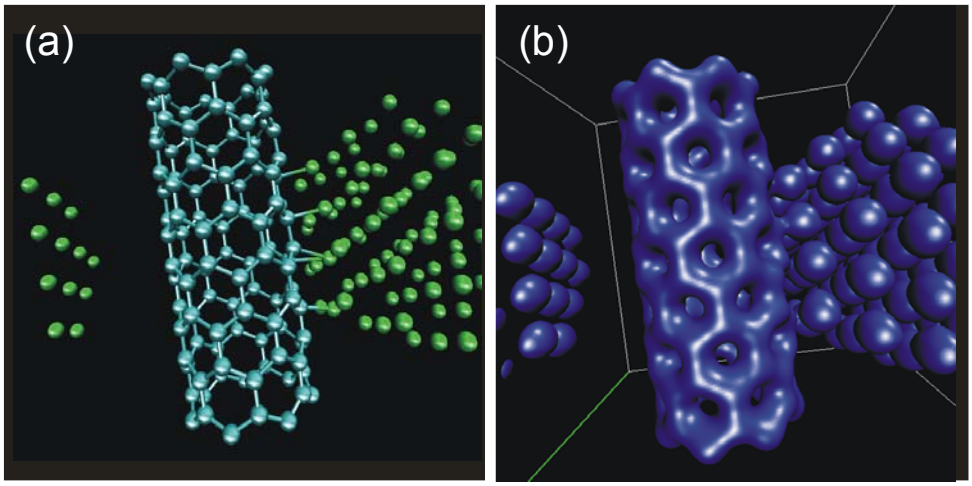

Figure S2: Atomic structure (a) and electron density (b) of a (7,0) nanotube and a 98 atom Fe cluster attached to the tube as revealed by DFT simulations. The atoms on the left-hand side belong to the cluster (periodic boundary conditions were used). It is evident that weak covalent bonds (about 0.4 eV per carbon atom in the contact area) were formed.

Summary of the results of atomistic simulations of junction formation:

A summary of our DFT and AP simulations is presented in table S1. The notations are partly explained in Fig. S3, and the values per bond are calculated by dividing the corresponding total energy by the number of bonds. The corresponding energy differences are shown in Fig. S3. We stress that the nanotube is not cut by the beam during the junction formation process; this configuration can be viewed as the limiting case which is useful for assessing the energetics of the process.

SWNT	N atoms	method	E_{cut} (eV)	N bonds	E_{C-C}^{bond} (eV)	$E_{rel}^{(1)}$ (eV)	E_{rel} (eV)	E_{C-M}^{bond} (eV)	$E_{C-C}^{bond} - 2E_{C-M}^{bond}$ (eV)
(7,0)	Fe 55	DFT	43.7	7	6.2	43.2	86.4	6.2	-6.1*
(7,0)	Fe 92	DFT	43.7	7	6.2	20.2	40.2	2.9	0.5
(7,0)	Fe 116	DFT	43.7	7	6.2	23.6	47.2	3.4	-0.5
(8,0)	Fe 200	DFT	49.9	8	6.2	20.5	41.0	2.6	1.1
(7,0)	Co 55	DFT	43.7	7	6.2	40.7	81.4	5.8	-5.4*
(7,0)	Co 116	DFT	43.7	7	6.2	22.8	45.6	3.3	-0.3
(7,0)	Fe 92	AP	27.4	7	3.9	10.5	21.0	1.5	0.9
(7,0)	Fe 116	AP	27.4	7	3.9	9.5	19	1.4	1.1
(10,0)	Fe 864	AP	39.3	10	3.9	13.5	27.0	2.7	1.2
(10,0)	Fe 672	AP	39.3	10	3.9	11.7	23.3	2.3	1.6
(6,6)	Fe 490	AP	46.8	12	3.9	6.5	13.1	1.1	2.8
(8,4)	Fe 490	AP	45.0	12	3.8	6.5	13.1	1,1	2.7

Table S1: Summary of our DFT and AP simulations

*These values are anomalously low, as the 55 atom cluster is very small and can easily be deformed due to new carbon-metal bonds.

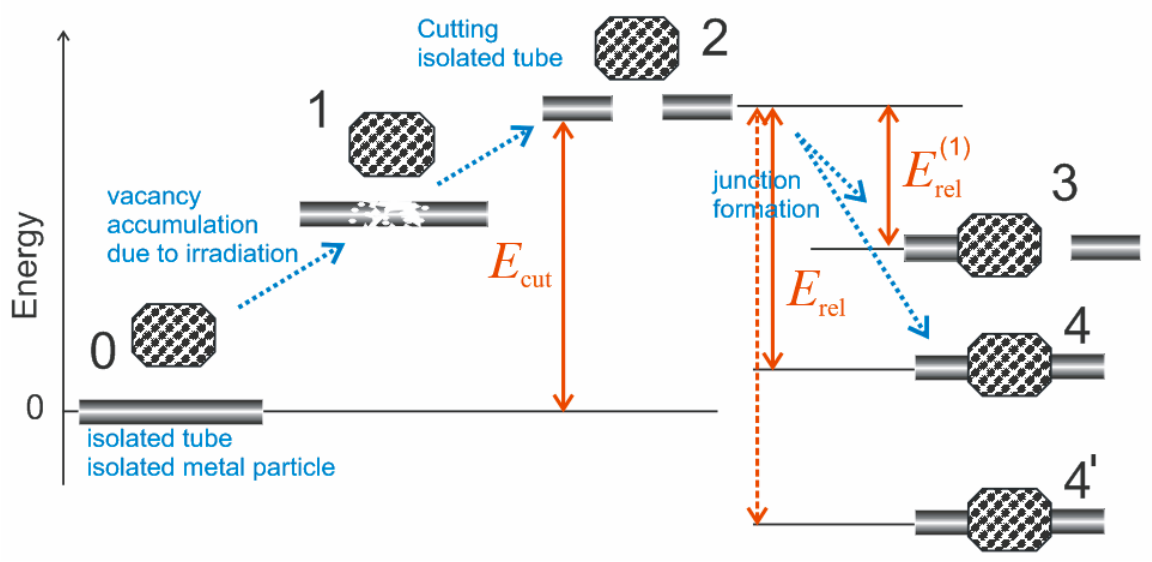

Figure S3: Energy diagram illustrating the energetics of a carbon nanotube-metal particle system under electron irradiation. Configuration "0" (the initial configuration) corresponding to an isolated SWNT plus isolated metal particle is taken as a reference. Electron irradiation creates vacancies in the nanotube, as illustrated in conf. "1". This is accompanied by an increase in the average potential energy of atoms in the junction area. The process of junction formation can be represented a sequence of configurations corresponding to a nanotube cut into two pieces (it is assumed that all the vacancies are localized in the same area), Conf "2". Finally the junction is formed, conf. "4" (or 4'), the final configuration.

References

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