

MATERIALS SCIENCE

Imaging an unsupported metal–metal bond in dirhenium molecules at the atomic scale

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Metallic bonds remain one of the most important and least understood of the chemical bonds. In this study, we generated Re₂ molecules in which the Re–Re core is unsupported by ligands. Real-time imaging of the atomic-scale dynamics of Re₂ adsorbed on a graphitic lattice allows direct measurement of Re–Re bond lengths for individual molecules that changes in discrete steps correlating with bond order from one to four. Direct imaging of the Re–Re bond breaking process reveals a new bonding state with the bond order less than one and a high-amplitude vibrational stretch, preceding the bond dissociation. The methodology, based on aberration-corrected transmission electron microscopy imaging, is shown to be a powerful analytical tool for the investigation of dynamics of metallic bonding at the atomic level.

INTRODUCTION

Bonding between metal atoms is of fundamental importance to many areas of science and technology, including catalysis and magnetism (1), and since the discovery of the Re–Re quadruple bond in [Re₂X₈]²⁻ in 1964 (2, 3), the global effort in understanding the nature of the metal–metal (M–M) bond has been growing strongly (1). The key challenge is to establish the bond order of M–M, which can vary from one to five and determines fundamental physical and chemical properties (1). Spectroscopy methods such as nuclear magnetic resonance, infrared spectroscopy, ultraviolet-visible spectroscopy, and x-ray diffraction are typically used (4–6). The latter is particularly important, as it allows measurement of the M–M bond length, which is inversely proportional to the bond order. However, unlike bonds between nonmetallic elements, M–M bonds are very sensitive to ligands around the metals (7, 8), creating the uncertainty whether the bond length and bond order reflect on the fundamental chemistry of the metals atoms or result from the effects of ligands, packing of molecules in the crystal or other external factors not related to the intrinsic M–M bonding. Encouraged by theoretical calculations predicting stable unsupported M–M bonds (9, 10), the existence of homonuclear intermetallic bonds has been experimentally demonstrated in the noble gas matrices under cryogenic conditions (11, 12), and more recently, the excited-state heteronuclear alkali metal diatomic molecule has been successfully obtained by combining two atoms with optical tweezers (13).

In this work, we create dirhenium molecules with unsupported Re–Re bonds using single-walled carbon nanotubes (SWNTs) as a nano-test tube while simultaneously imaging their structure and dynamics on the level of the single atom in real time using state-of-the-art chromatic and spherical aberration-corrected (C_c/C_s-corrected) SALVE (Sub Angstrom Low-Voltage Electron Microscopy) transmission electron microscopy (TEM) (14, 15). Moving freely at room temperature along the SWNT, the Re₂ molecules have been shown to switch bond order between one, two, and four, and we

could follow the process of dissociation and reformation of inter-metallic bonds in individual Re₂ molecules.

RESULTS

Dirhenium molecules are generated from Re₂(CO)₁₀ compound inserted into SWNTs, followed by thermal or e⁻-beam-induced elimination of CO ligands (Fig. 1A). The dissociation of Re₂(CO)₁₀ molecules and the removal of CO ligands is confirmed by Fourier transform infrared spectroscopy (FTIR) measurements (fig. S1). If several precursor molecules Re₂(CO)₁₀ are agglomerated in the nanotube, they form a metal nanocluster with several Re atoms under these conditions (16, 17); in the case of a single isolated molecule, Re₂(CO)₁₀ ligand elimination yields a well-defined Re₂ molecule as observed by aberration-corrected high-resolution TEM (AC-HRTEM) (three typical images of Re₂ are shown in Fig. 1A). Two individual dirhenium molecules can be observed in the same SWNT in the top AC-HRTEM image of Fig. 1A. Monitoring an individual Re₂ by time-series 80-kV AC-HRTEM imaging (Fig. 1B) shows that the two Re atoms are bonded to each other within the dirhenium molecule, as Re₂ moves as a whole in the cavity of SWNT, which differs notably from the dynamics of individual heavy atoms in graphitic structures that move by hopping from one vacancy defect in the carbon lattice to another under e-beam irradiation (18–21). The Re–Re bond ensures that the movement of both atoms is correlated, and the dirhenium molecule takes positions in the SWNT, consistent with small number of possible orientations: (i) chemisorbed standing (20 s), (ii) chemisorbed lying (0 s), and (iii) successive chemisorbed standing and lying configurations during the exposure time (26 s) (Fig. 1B). The same Re₂ molecule is able to change its position and orientation over the duration of the experiment. This process is stimulated by the e⁻-beam serving as both a source of energy and the imaging probe, as the kinetic energy of the incident electrons is transferred to the Re atoms (directly ~1.0 eV and via carbon atom ~14.7 eV). As the positions of the rhenium atoms are monitored continually during the exposure time of each frame (1 s), the motion of Re₂ switching from one orientation to another can be captured within a single frame and analyzed (see Fig. 2). For example, it is possible to discern that the change in the bonding orientation that takes place during the 26th second corresponds to a change from

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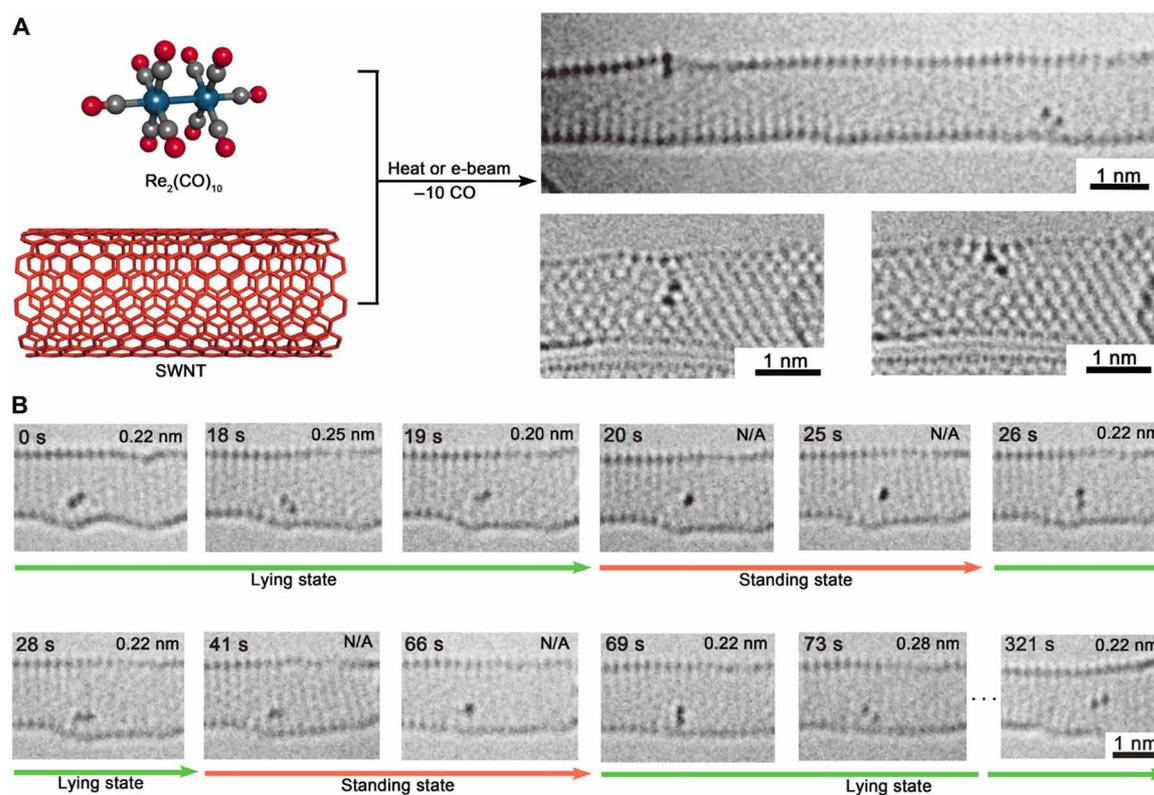


Fig. 1. Diatomic molecule Re_2 trapped in carbon nano-test tube. (A) Schematic illustration of the preparation of dirhenium molecule confined in SWNT by eliminating CO groups from $\text{Re}_2(\text{CO})_{10}$ precursor. Three dirhenium molecules in two SWNTs can be observed in the AC-HRTEM images [two dirhenium molecules imaged at 80 kV with Cs-corrected (top image) and one dirhenium molecule Cc/Cs-corrected (bottom two images) TEM, unprocessed data]. (B) Time-series AC-HRTEM images (80 kV) from movie S1 acquired by Titan Cs-corrected TEM showing the characteristic states of the dirhenium molecule changing under e⁻ beam irradiation. This dirhenium molecule is the right one in the SWNT of the top AC-HRTEM image in (A) named “Titan Re_2 A.” The corrected Re–Re bond length of each frame is presented; error is ± 0.015 nm. N/A is the standing state with unknown bond length.

the initial standing orientation lasting 0.29 s into the lying orientation lasting 0.71 s in the 1.0 s frame (fig. S2).

DISCUSSION

There is a well-known strong inverse correlation between the M–M bond length and bond order (3). The Re–Re single σ bond length in $\text{Re}_2(\text{CO})_{10}$ is 0.304 nm for the free molecule and 0.302 nm in the crystal (22). However, in our experiments, after the CO ligands have been removed, the Re–Re bond measures 0.220 nm (± 0.015 nm) at the initial state (0 s; Fig. 1B), indicating that the bond order is close to four, as it agrees well with the length of a quadruple Re–Re bond in $[\text{Re}_2\text{X}_8]^{2-}$ of 0.224 nm (2). Our density functional theory (DFT) calculations for Re_2 match well with the experimentally observed distances, predicting Re–Re bond lengths of 0.21 nm for a free (nonbonded) Re_2 and approximately 0.22 nm for the dirhenium molecule bound to the SWNT wall by the stable standing orientation. Because the SWNTs are cylindrical surfaces, all the bond lengths quoted in this work are corrected from the directly measured projected distance using the method described in fig. S3. Statistical analysis of Re–Re bond lengths in 226 frames from 0 to 553 s (Fig. 2C) shows three major values of the length of 0.22, 0.25, and 0.30 nm, occurring with 44, 24, and 11% probability (Fig. 2E). The nonrandom, discrete values assumed by the Re–Re bond are likely to be correlated with the quadruple bond, double bond, and single

bond, respectively, which were previously reported from bulk measurements on various complexes containing a Re_2 core (3, 22). In additional 18% of the cases, the bond length cannot be measured as marked “N/A,” as the “standing” state is aligned with the direction of the electron beam. Being limited by the spatial resolution of only spherical AC-TEM, the atomic structure of the SWNT and hence the precise position of the Re atoms with respect to the carbon lattice remain unresolved.

With the help of the Cc/Cs-corrected SALVE TEM, the e⁻ beam-stimulated dynamics of dirhenium molecule are recorded with a much higher spatial resolution, as shown in movie S2. A Re_2 molecule can be observed standing at defective sites on the top SWNT of two parallel SWNTs at the initial state (0 s; Fig. 2A shows the first stage of movie S2 from 0 to 87 s). A van der Waals (vdW) gap of 0.3 nm is formed by the two parallel SWNTs with different chirality. In the first 50 s, Re_2 shows similar behavior to the Re_2 in Fig. 1B, switching between multiple different orientations at the defective site. An intact SWNT is impermeable to almost all atoms and ions except H⁺ (23). However, a vacancy defect on the SWNT could provide a channel for atoms to penetrate. At 50 s, one Re atom of the dirhenium molecule goes across the upper wall of the host SWNT from the defective site. In the following 20 s, the whole dirhenium molecule climbs out and starts drifting along the outer surface of the host SWNT, driven by stronger bonding of the metal with defect from outside, as was predicted by dynamic simulations

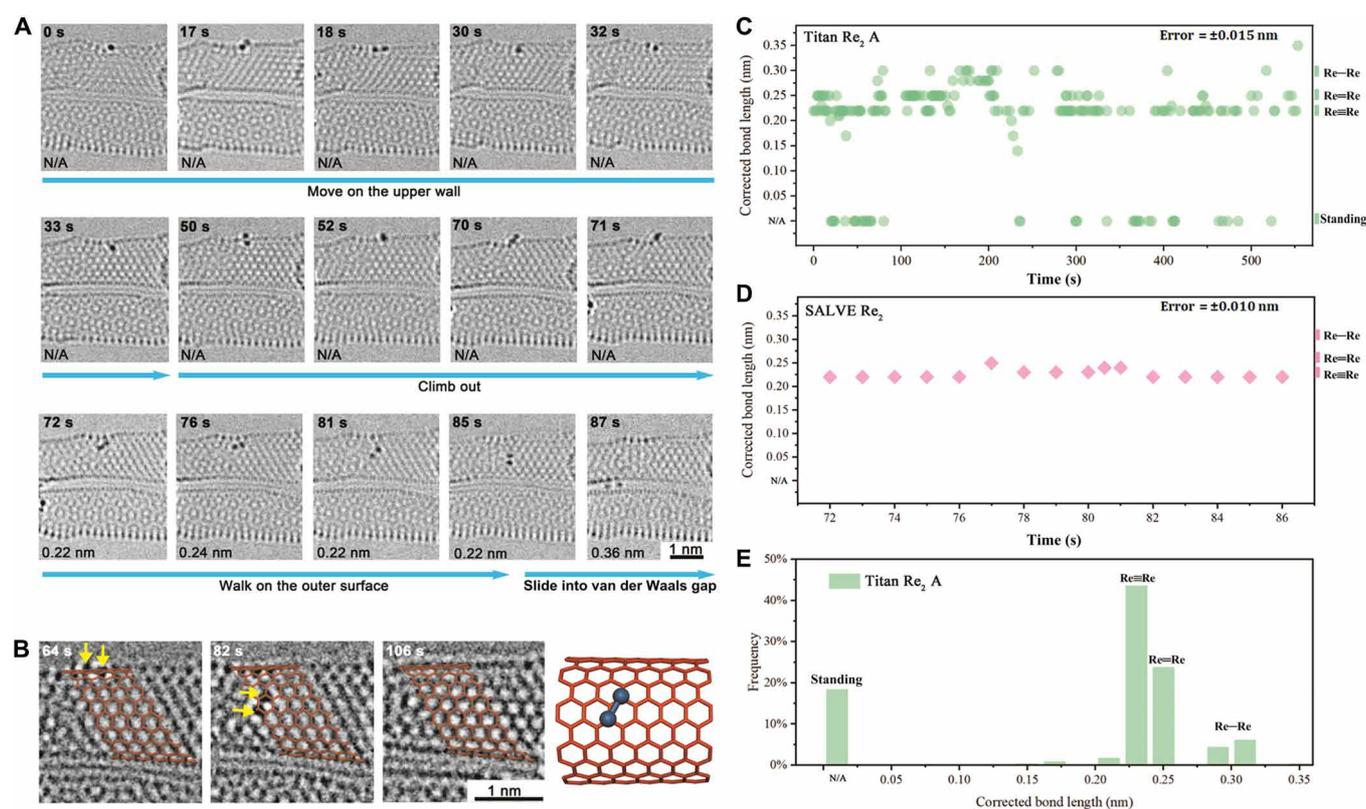


Fig. 2. Changes in Re–Re bond length over time. (A) Time-series AC-HRTEM images (80 kV) (unprocessed data) of the first stage of movie S2 acquired by the SALVE TEM. At this stage, the dirhenium molecule moves at a defect site on the SWNT, climbs out from the defect, and then slides into the vdW gap between two parallel SWNTs. The corrected Re–Re bond length of each frame is presented; error is ± 0.010 nm. (B) Selected frames with adjusted high contrast from movie S2 for analyzing the atomically precise position of the dirhenium molecule when it is drifting along the outer surface of host SWNT. The position of the Re atoms are indicated by yellow arrows. The AC-HRTEM images are partially covered by the model of an SWNT with chirality of (10, 10). The simulated structure shows the position of dirhenium molecule in the frame of 82 s. (C) Corrected bond length changing of the right dirhenium molecule in movie S1 (Titan Re₂ A); error is ± 0.015 nm. (D) Corrected bond length of the dirhenium molecule drifting along the outer wall of SWNT in movie S2 (SALVE Re₂); error is ± 0.010 nm. (E) The histogram shows the count frequencies of the different bond lengths of Titan Re₂ A (0 to 553 s).

(24). From 72 to 85 s, the dirhenium molecule drifts along the outer surface of the host SWNT and then slides into the one-dimensional vdW gap, as indicated by yellow arrows (Fig. 2B). The simulated structure in the right of Fig. 2B shows an atomic structure of the lying orientation of dirhenium molecule in the AC-HRTEM image of 82 s with a Re–Re bond length of 0.22 nm. Figure 2D only shows the bond length changing of the dirhenium molecule when it is drifting along the outer wall before it slides into the vdW gap (72 to 85 s), because the real bond length of Re₂ moving and rotating at the defect site is immeasurable. According to the analysis of the bond length distribution measured over time for the dirhenium molecules (Fig. 2, C to E), the lying orientation with corrected Re–Re bond length of 0.22 nm and the standing orientation with immeasurable bond length are the most common bond structures observed in these two time series, although bond lengths of 0.25 and 0.30 nm are also observed. The measured metallic bond length changes in discrete steps, indicating the existence of single and double Re–Re bonds (Fig. 2C).

The vdW gap between the two parallel SWNTs in the initial state of the second stage (89 s in Fig. 3A) is approximately 0.32 nm (± 0.010 nm), consistent with the theoretical prediction by Lennard-Jones model (25). This vdW gap confines Re₂ and provides a one-

dimensional channel in the vacuum, limiting Re₂ translation and rotation. In the first 7 s (87 to 94 s) after the dirhenium molecule moves into the vdW gap, the contrast of the Re atoms shows unusual symmetrically elongated features, indicating that the Re atoms are delocalized on the time frame of a single exposure (0.5 s), which may be caused by oscillations along the Re–Re bond, described as a stretch vibration (Fig. 3B). The center distance of the elongated spots is 0.36 nm, which is slightly longer than the Re–Re single bond (around 0.30 nm) in compounds (21), while the amplitude of the oscillation of Re atoms is ± 0.04 nm. After oscillating for 7 s, Re₂ breaks into two unbound Re atoms with a distance of 0.58 nm (94 s in Fig. 3A and the second column in Fig. 3B). After the separation, the contrast of two Re atoms is no longer elongated and becomes near round. This observation indicates that once the Re–Re bond length exceeds that of a single bond, the molecule may exist in an excited state manifested in a large amplitude of vibrations, and that beyond this critical point, the bond breaks and the two metal atoms separate. In our experiments, Re₂ trapped in the one-dimensional vdW gap acts like a harmonic oscillator, pumped with the kinetic energy transferred from the 80-keV electrons to the Re atom, until it is large enough to overcome the barrier of Re–Re bond dissociation (at 94 s in Fig. 3A). The two Re atoms move freely in the one-dimensional

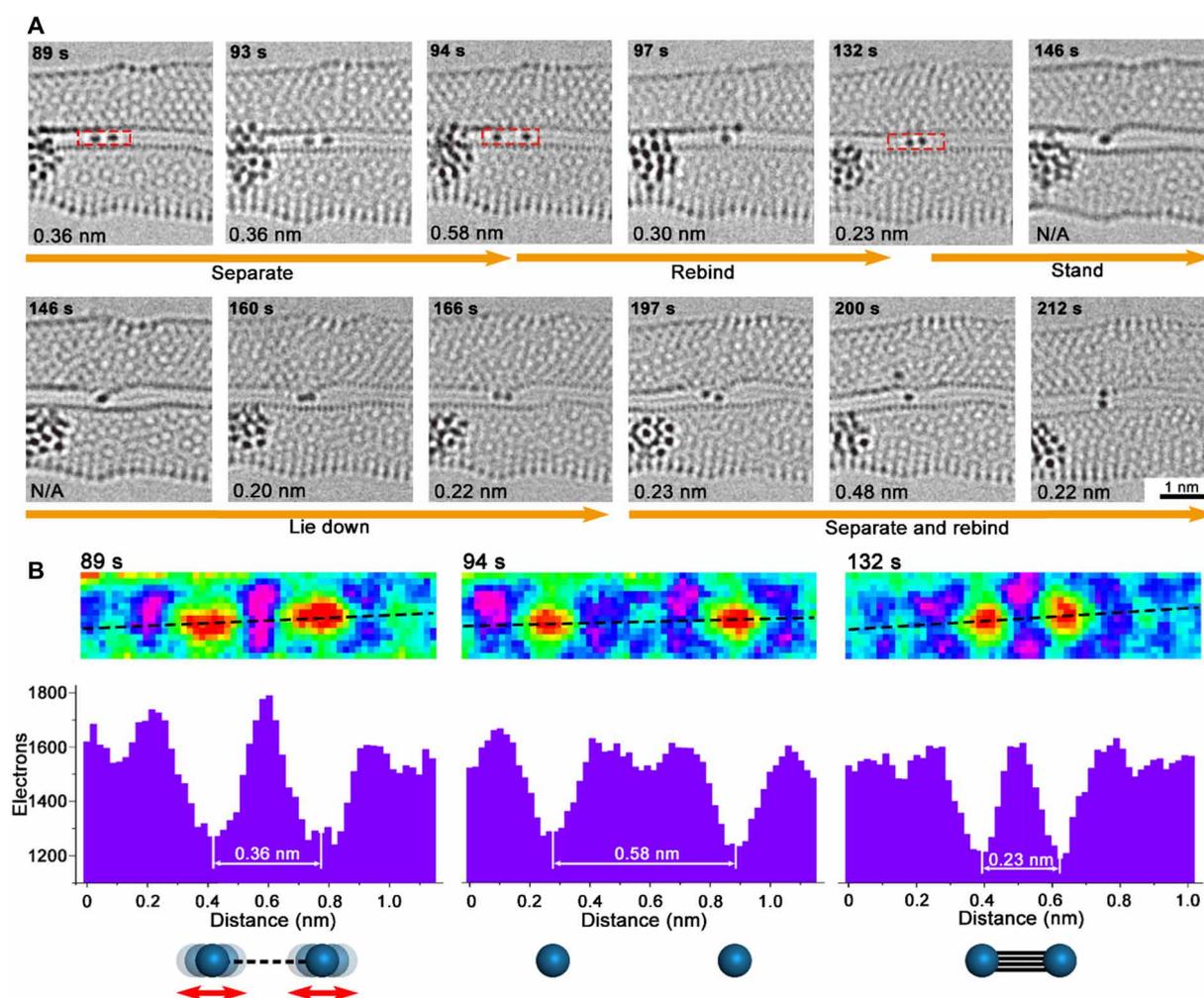


Fig. 3. Atomic-scale dynamics of Re-Re bond dissociation. (A) Time-series AC-HRTEM images (80 kV) (unprocessed data) of the second stage of movie S2 acquired by the SALVE TEM. At this stage, the dirhenium molecule confined in the vdW gap shows various dynamic processes. The metallic bonds between two Re atoms break and rebind twice. The dirhenium molecule also stands and lies down in the gap. (B) In the first row, false-color images of the red dashed line framed areas in the AC-HRTEM images of 89, 94, and 132 s in (A). The second row shows the intensity profiles of the corresponding black dashed line in the false-color images of the same column. The distances between two Re atoms are measured with an error of ± 0.010 nm. The third row shows the possible state of the two Re atoms in each image of the first row.

vdW gap until they collide and recombine into Re_2 at 97 s. The bond distance of the reformed Re_2 reduces from 0.30 (97 s) to 0.23 nm (132 s). The contrast of two Re atoms in the frame of 132 s are near round with a distance of 0.23 nm, indicating that the two Re atoms are bound again by a quadruple bond. This reformed dirhenium molecule shows the same properties as before, moving between different orientations in the one-dimensional vdW gap in the following 34 s, similar to the behavior inside and on the SWNT. In addition, the free Re atom is chemically active toward SWNT, as shown in our previous work (26), and interacts with the upper SWNT restructuring the carbon lattice at 97 s. At 200 s, Re_2 dissociates again and recombines at 212 s. This dirhenium molecule moves in the vdW gap in the following 181 s and merges into the large Re cluster in the lower SWNT as shown in movie S2.

DFT calculations have been carried out to elucidate the stable configurations and electronic structure of Re_2 bonded to SWNT (Fig. 4). As discussed in Materials and Methods, a search of possible stable bonding configurations inside the SWNT revealed only the

presence of a single standing mode with a Re-Re bond length of 0.22 nm, in which Re_2 bonds in an η^6 -mode to all six carbon atoms of a single hexagon with a “4 + 2” asymmetry introduced by the curvature of the nanotube wall. The binding energy of this configuration is -165 kJ/mol (-1.71 eV), relative to the separated dirhenium molecule and SWNT. On the outside of the nanotube, the η^6 -standing configuration is again found to be the lowest energy orientation, but the change in curvature introduces several stable lying configurations, which are local minima at higher energy, geometrically and energetically similar to one another (fig. S7).

To understand the bonding configurations observed, it is instructive to examine the spatial extent of the molecular orbitals involved in the bonding. The atomic Re orbitals and the occupied and low-lying unoccupied orbitals of Re_2 are presented in fig. S4, and the electronic structure of the dirhenium molecule is discussed in more detail in the Supplementary Materials. The highest occupied molecular orbital (HOMO) [singly occupied molecular orbital (SOMO)] of the bound species in the standing configuration corresponds to the HOMO

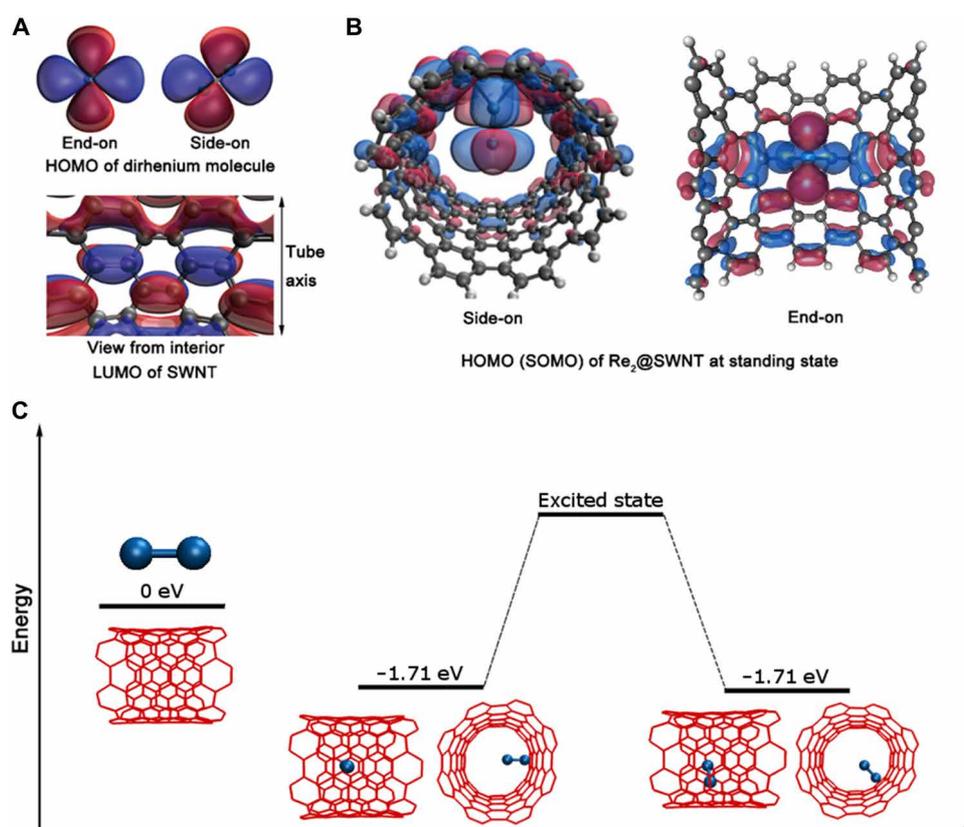


Fig. 4. Interactions of Re_2 with carbon nanotube. (A) Comparison of the spatial extent of the Re_2 HOMO (SOMO) viewed end-on and side-on; the overlap with electron density of the SWNT LUMO sufficient for bonding is only achieved when Re_2 approaches the nanotube wall in the end-on orientation. (B) Side-on and end-on views of the HOMO (SOMO) of the bound configuration, showing the contraction of the (blue) orbital lobes that maximizes bonding overlap (in the end-on view, some carbon atoms have been removed and the electron density isovalue has been increased to aid visualization). (C) Illustration of the dynamics of the dirhenium molecule in the SWNT, with the associated calculated energies relative to the separated molecule and SWNT (left), and front and side views of each state.

(SOMO) of the isolated Re_2 , but with contraction of the orbital lobes that are perpendicular to the nanotube axis (Fig. 4B). This maximizes the overlap with the two carbon atoms that are closer to the dirhenium due to the curvature-induced $4 + 2$ asymmetry (shown in blue in Fig. 4A). The “end-on” standing η^6 -bonding is more stable than “side-on” lying bonding, as this provides a better orbital overlap between the Re_2 HOMO and the SWNT LUMO, in terms of size, shape, and ease of the above orbital contraction. On the outside of the SWNT, the rhenium dimer encounters the convex curvature of the nanotube, and two carbon atoms lie further from the dimer than the other four. The orbital contraction is therefore less pronounced, and the larger orbital lobes presented by the side-on orientation of dirhenium are able to take part in stable bonding with the nanotube wall. Note that the curvature of the SWNT wall is, in turn, affected by the dirhenium molecule, exhibiting a slight flattening of the wall in the region of the bonding, as can be seen in the side views in Fig. 4C. Our calculations predict the presence of standing configurations inside the nanotube; the presence of stable lying configurations could be caused by the different curvature of SWNTs with different diameters. As the bonding modes available to Re_2 seem to be largely influenced by the curvature of the SWNT wall, it is reasonable to assume that the wider nanotube with a smaller degree of curvature imposes less of a restriction on the possible bonding modes and behaves more similarly to the outside of the tube. In

addition, the presence of defects and deformations in the SWNT under electron irradiation were not considered in our simulations but may affect the bonding between dirhenium and the SWNT.

Using our experimental observations in conjunction with the theoretical modeling, Fig. 4C illustrates a plausible energy profile for the movement of Re_2 along the nanotube. We propose that, upon elimination of the CO ligands from the precursor molecule, Re_2 bonds to the interior of the SWNT wall, a process we predict to be strongly thermodynamically (-165 kJ/mol binding energy) and kinetically (no energy barrier) favorable. On the order of seconds in our conditions, the electron beam transfers energy to excite Re_2 , from which the molecule can relax into adjacent energy minima (Fig. 4C). The absence of any local minima in which Re_2 exists inside the SWNT without being bonded to the walls explains the observed stepwise motion of the dirhenium molecule under electron irradiation, as these would result in a more long-range migration process.

We show that the simultaneous function of the electron beam as a source of energy and an imaging tool allows advancement in the understanding of metallic bonding. The rhenium homonuclear diatomic molecules Re_2 are created in nanotubes in situ under AC-HRTEM observation, and dynamics of Re_2 are imaged with atomic resolution. The metallic bond can change over time as a result of the electron beam effect, most frequently adopting a quadruple bond order. Re_2 can reversibly dissociate to independent atoms under

the electron beam, which transfers up to ~ 1 eV (~ 100 kJ/mol) to a Re atom, directly observed when the molecule is confined in the one-dimensional gap between two parallel NTs. An unexpected bonding state where the Re-Re bond order is less than one, accompanied with a large amplitude of vibration observed just before the bond dissociation, indicates the existence of previously unknown bonding states between metal atoms. A combination of DFT calculations and AC-HRTEM time-resolved experiments sheds light on the atomistic mechanism of metallic bond dynamics in real time and direct space, opening up avenues for discovery of new inorganic and organometallic species by electron microscopy methods, such as predicted W_2 with quintuple bond or Re_3 clusters, and exploration of their physical properties and chemical reactivity at the level of the single atom.

MATERIALS AND METHODS

Synthesis of dirhenium molecules confined in SWNTs

SWNTs (Carbon Solutions, USA) were thermally treated to open the ends of the nanotubes and to remove the residual amorphous carbon from the outer walls of the SWNTs before use. The as-received SWNTs were heated in air for 30 min at 600°C with a weight loss of approximately 30% observed for samples. The freshly opened SWNTs were mixed with a twofold by weight excess of $Re_2(CO)_{10}$ compound (Sigma-Aldrich). The resultant mixture was then sealed in a Pyrex glass tube under reduced pressure (10^{-6} mbar) and heated to 150°C for 3 days. The sample was then rapidly cooled to room temperature, and the SWNTs were washed with tetrahydrofuran (100 ml) to remove any species from the outside of the nanotube and filtered through a polytetrafluoroethylene membrane (pore size = $0.2\ \mu\text{m}$). The sample was then dispersed in isopropanol and drop cast onto a lacey carbon-coated copper TEM grid for HRTEM analysis. The formation of dirhenium molecules can also be achieved by heating $Re_2(CO)_{10}@SWNT$ at high temperature. This was achieved by sealing $Re_2(CO)_{10}@SWNT$ under argon in a Pyrex tube and heating at 500°C for 3 hours. Rhenium cluster@SWNT samples prepared in this way were identical to the samples formed via electron beam-induced elimination of CO ligands from $Re_2(CO)_{10}$. FTIR measurement shown in fig. S1 confirms the removal of CO from nanotubes during the heating process.

Electron microscopy

AC-HRTEM images in movie S1 were carried out using an image side C_S -corrected FEI Titan 80-300 TEM operated at 80 kV accelerating voltage with a modified filament extraction voltage for information limit enhancement. Images were recorded on a slow-scan charge-coupled device camera type Gatan UltraScan 1000XP. Because a certain amount of electron dose was required to achieve atomic resolution, the exposure time for each frame was 1.0 s. The dose rate of e-beam applied in movie S1 was $1.05 \times 10^8\ \text{e}^- \text{nm}^{-2}\ \text{s}^{-1}$.

AC-HRTEM images in movie S2 were carried out using the image side C_C/C_S -corrected SALVE instrument (20 to 80 kV) operated at 80 kV accelerating voltage with a point resolution of $<0.08\ \text{nm}$. The exposure time for the frames in movie S2 was 0.5 s. The dose rate of e-beam applied in movie S1 was $1.05 \times 10^8\ \text{e}^- \text{nm}^{-2}\ \text{s}^{-1}$. The dose rate of e-beam applied in movie S2 was $1.10 \times 10^8\ \text{e}^- \text{nm}^{-2}\ \text{s}^{-1}$.

For each observation, approximately 30 s were spent for adjusting the magnification, dose rate, and focal length. All imaging experiments were carried out at room temperature. In addition, 26 s (from

252 to 278 s) was spent for centering the drifted SWNT in movie S1 during continuous irradiation.

Computational methods

DFT simulations were performed to find stable bonding configurations of the dirhenium molecule with the host SWNT. Rhenium atoms were modeled with the BLYP/SRSC functional/effective core potential pairing, with carbon and hydrogen atoms modeled with a BLYP/6-31G* functional/basis set pairing for initial geometry optimizations, followed by optimizations using BLYP/6-311G* (see the Supplementary Materials for more information on the choice of DFT method). Grimme's empirical DFT-D3(BJ) model (27) was used to account for the effects of dispersion. The reported binding energy was corrected for basis set superposition error by using the counterpoise method. The hydrogenated (8,8) SWNT shown in fig. S6 was used as a model nanotube, with a diameter of 1.1 nm compared to the experimental (16,1) SWNT with a diameter of 1.3 nm. The optimized rhenium dimer was placed in initial positions corresponding to those in fig. S5 as well as several different nonbonded positions in the center of the SWNT, and all atom positions (including Re_2) were fully optimized. On the inside of the SWNT, all optimizations resulted in the formation of a standing bonding configuration centered over a hexagon in the tube (shown in Fig. 4). On the outside of the tube, the equivalent hexagon-centered standing bonding configuration was the lowest energy structure, but there were also several additional bonding configurations (shown in fig. S7). The Mulliken charge distribution of the bonded standing state found in the DFT calculations is shown in fig. S8.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/6/3/eaay5849/DC1>

Section S1. Re_2 electronic structure and choice of functional

Fig. S1. Infrared spectra of Re_2 precursor before and after removal of CO ligands.

Fig. S2. Analysis of a typical migration process repeatedly observed in our TEM experiment.

Fig. S3. Schematic diagram explaining the method for calculating the real bond length between two Re atoms in Re_2 by correcting the measured projected bond length.

Fig. S4. Shapes and energies of Re_2 orbitals.

Fig. S5. Possible configurations of Re_2 lying on the graphitic structure.

Fig. S6. The model SWNT system used in the DFT calculations discussed in the text.

Fig. S7. Configurations of Re_2 outside SWNT with respect to the nanotube lattice.

Fig. S8. The Mulliken charge distribution of the bonded standing state found in the DFT calculations.

Movie S1. Dynamics of two Re_2 molecules confined in SWNT stimulated and imaged by electron beam in Titan TEM at 80 kV.

Movie S2. Dynamics of one Re_2 molecule stimulated and imaged by electron beam in SALVE TEM at 80 kV.

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