

# Supporting Information

## Atomic Scale Imaging of Reversible Ring Cyclization in Graphene Nanoconstrictions

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Figure S1. Reversible cyclization of short carbon chains

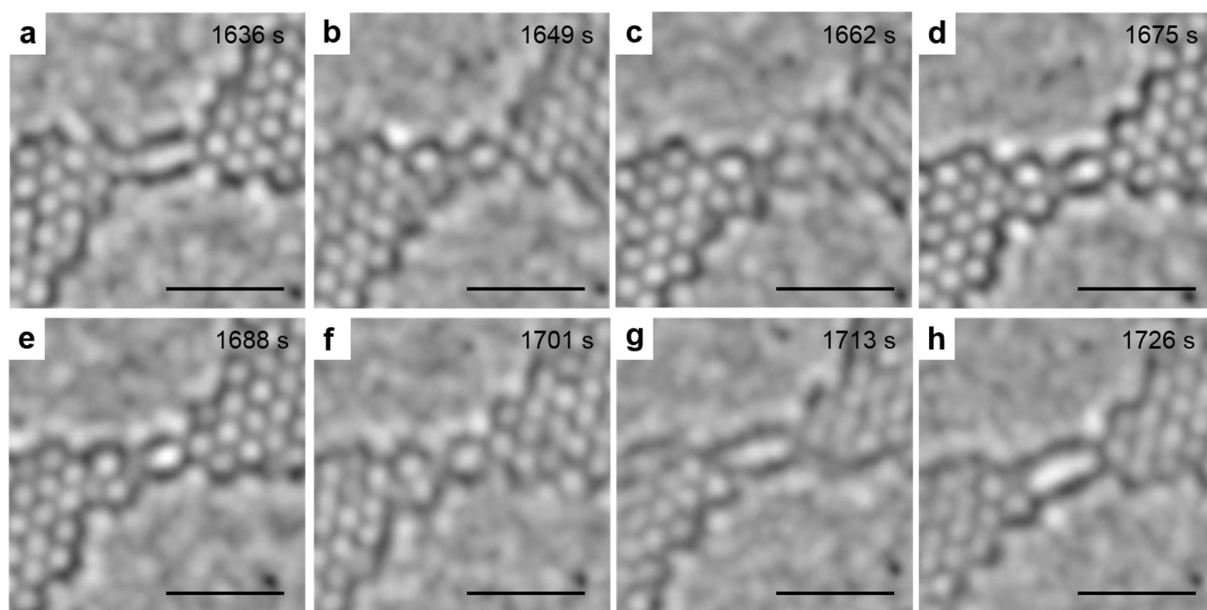
Figure S2. DFT calculation on hexagonal lattice versus two separate chains with applied strain

Figure S3. DFT calculation on the observed structure shown in the second frame image of Figure 4a according to the presence of hydrogen atoms

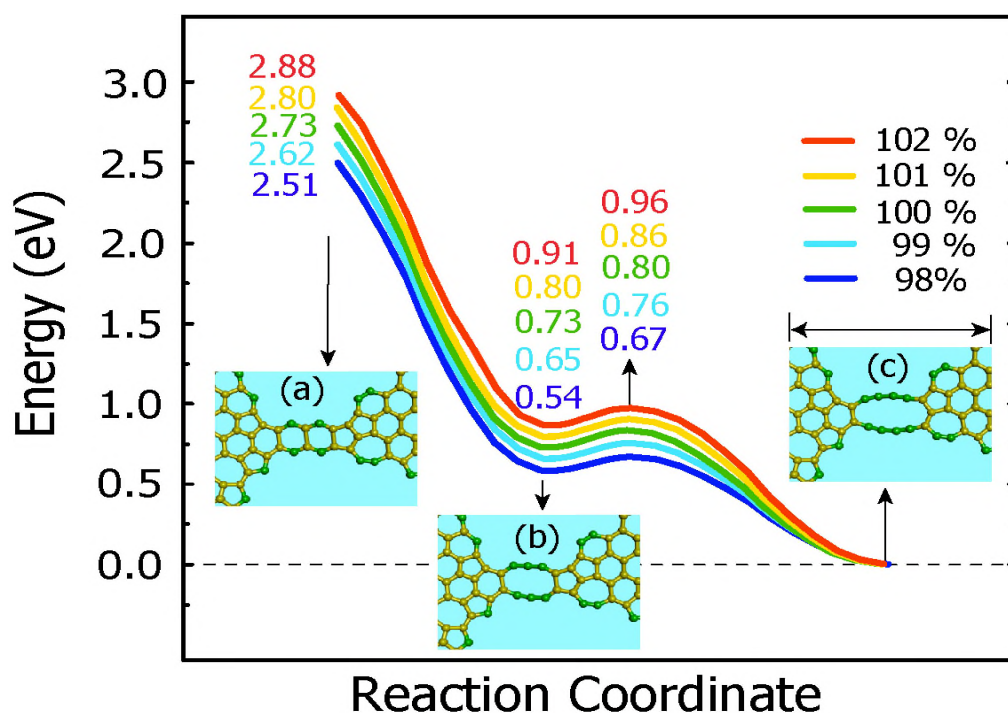
Figure S4. DFT calculation on the observed structure shown in the third frame image of Figure 4a according to the presence of hydrogen atoms

Figure S5. DFT calculation on various examples of structural changes in long carbon chains with hydrogen atoms involved

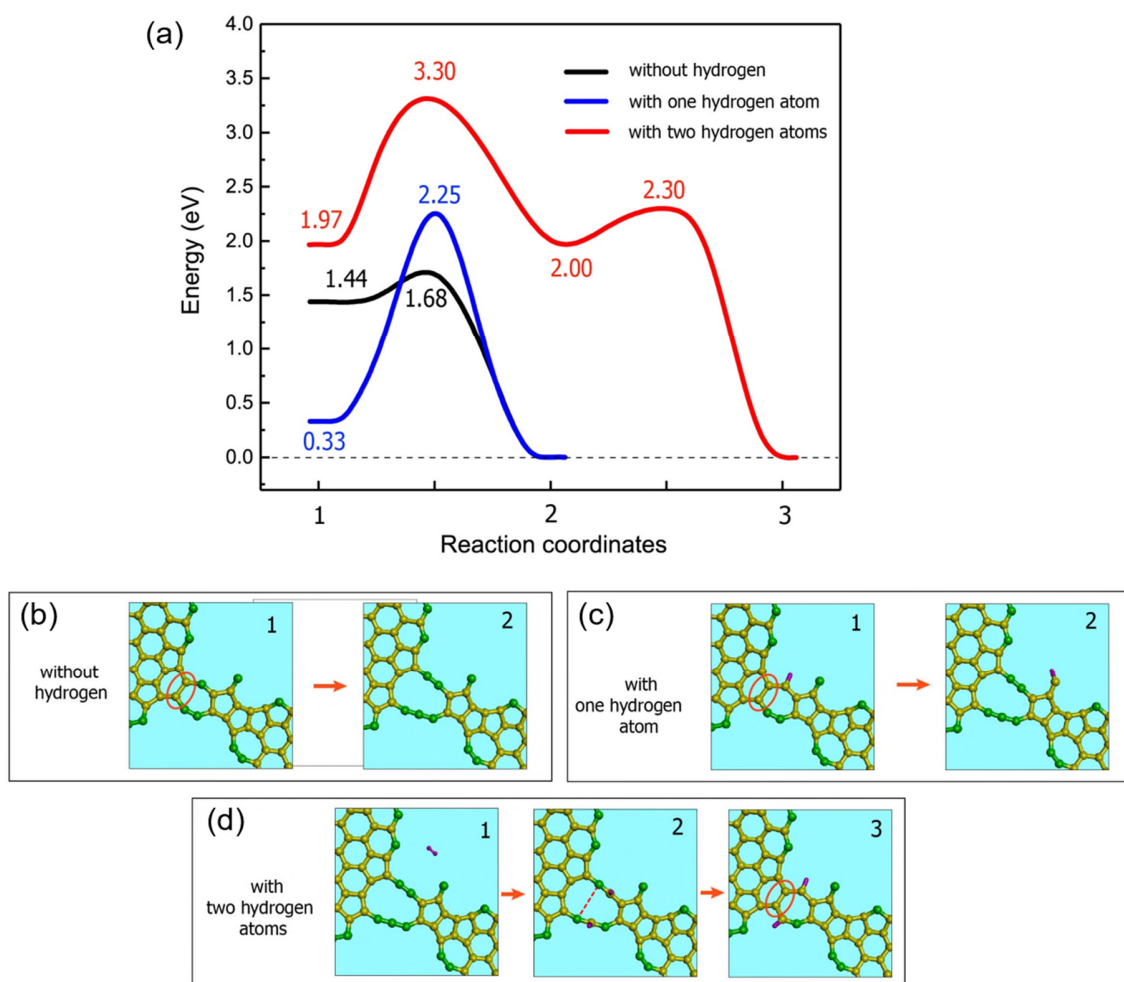
Figure S6. DFT energy curve showing the process of a complete ring closure from long carbon chains while more hydrogen atoms are attached



**Figure S1. Reversible opening and closing at a different short atomic double carbon chain position.** (a-h) Sequential AC-TEM frame images under the continuous electron-beam irradiation. The scale bar in each panel is 1 nm.

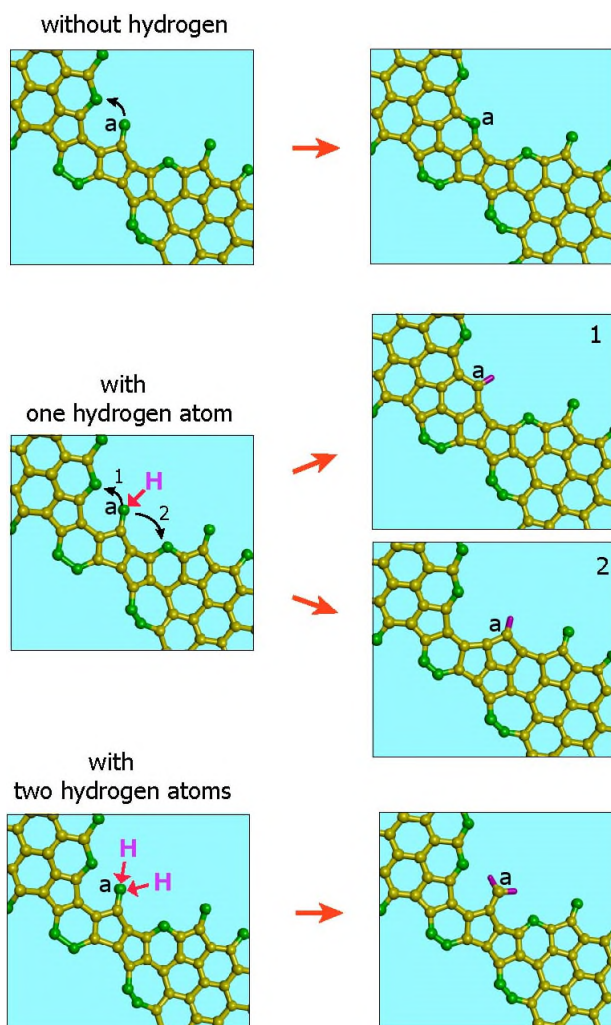


**Figure S2. The DFT energy curve depending on the applied strain for the process from a ring structure to short double carbon chains without hydrogen.** The green curve shows the energy curve of the structural transformation when the system is fully relaxed. The percentage values indicate the extension or contraction rate of the structure in (c) along its horizontal direction. The structure (a) is not stable and cannot be observed without hydrogen, therefore, it spontaneously transforms into more stable structures in (b) and (c). Because the energy barrier is also very small from (b) to (c), a pentagon at the right edge of short double chains easily open to form the final structure in (c). We varied the strain applied on the system, which does not affect the results.



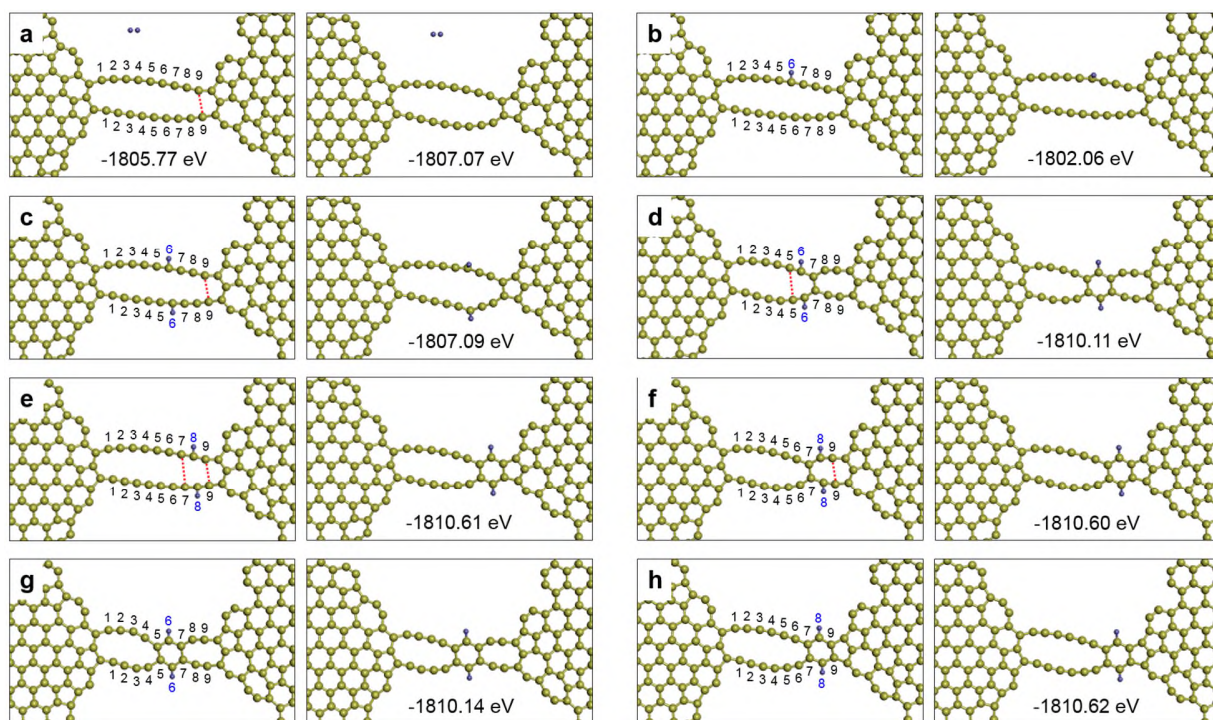
**Figure S3. The DFT calculation analysis for the AC-TEM image in the second frame of Figure 4a without hydrogen, with one hydrogen atom, and with two hydrogen atoms.** (a) The energy barrier plot relative to the reaction coordinates, where the integers 1, 2, and 3 in the x-axis correspond to each atomic configuration shown in (b), (c), and (d) (black curve: without hydrogen as in (b), blue curve: with one hydrogen atom as in (c), red curve: with two hydrogen atoms as in (d)). The numbers shown around each curve are energy values relative to the most stable structure in each case. The structure in (b)-1 is locally stable with a small energy barrier (0.24 eV) as shown in the black curve in (a). When the first order Arrhenius relation for the activation is considered, the carbon bond indicated by a red ellipse in (b)-1 is broken in  $10^{-6}$  sec and the structure changes into (b)-2 very fast. Therefore, without hydrogen, the structure in (b)-1 is not likely to be observed in AC-TEM images. In (c), with a hydrogen atom, even though the energy barrier to break a carbon bond increases to  $2.25 - 0.33 = 1.92$  eV, the initial structure in (c)-1 finally transforms to a more

stable structure as in (c)-2, once the energy barrier is overcome by electron beam ejection. However, with two hydrogen atoms, a carbon-carbon bonding is not broken and stable as shown in the final structure in (d)-3, which shows that our AC-TEM image in the second panel in Figure 4a is possible to be observed only when more than two hydrogen atoms are involved in the reaction system.



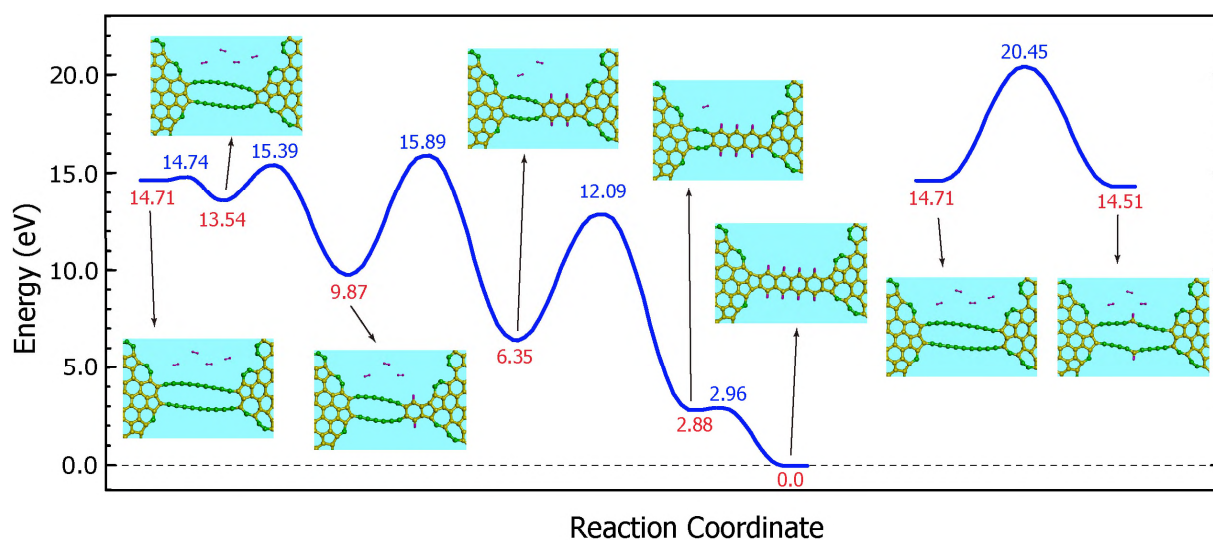
**Figure S4. The DFT calculation analysis for the AC-TEM image in the third frame of Figure 4a without hydrogen, with one hydrogen atom, and with two hydrogen atoms.** Without hydrogen, the carbon atom “a” forms a bond spontaneously with a neighbor carbon atom. With one hydrogen atom, the carbon atom “a” attached by hydrogen easily makes a bond either with left or right carbon atom. When two hydrogen atoms are attached to the carbon atom “a”, the

structure remains during the DFT structural relaxation. Therefore, the structure shown in the third AC-TEM image in Figure 4a can be observed in the involvement of at least two hydrogen atoms.



**Figure S5. The initial and final atomic structures of 9-atom length double carbon chains, when hydrogen atoms are involved in the DFT calculation.** Various atomic models of long double carbon chains are considered in the DFT calculation and represented with the total energy in each panel, regarding the attachment position and the number of hydrogen atoms (shaded in violet colour), along with a cross-linking or no bonding between the chains. Dotted red lines represent bond formations. **(a)** A hydrogen molecule is considered in the system, not forming any bonding with the chains. **(b)** One hydrogen atom is attached to the middle of the chain. **(c,d)** Two hydrogen atoms are attached to the middle of both chains, when there is **(c)** no bonding at the beginning and **(d)** a cross-linking is already formed in the initial state. **(e,f)** Two hydrogen atoms are attached near to the end of the chains, when there is **(e)** no bonding at the beginning and **(f)** a cross-linking is already formed in the initial state. **(g,h)** A hexagonal ring is formed and passivated by hydrogen atoms **(g)** in the middle and **(h)** near the edge of the chains.





**Figure S6. The DFT energy curve for the process from long double carbon chains to the ring structures when hydrogen atoms are gradually attached.** The atomic structures and curve on left hand side show a sequential ring closure process and the corresponding energies and barriers while more hydrogen atoms are attached to the carbon chains during the process. The right hand side shows the energy curve and structures in the case of dissociative adsorption of a hydrogen molecule on the center of the chains.