Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Materials for

Molecular Understanding of the Effect of Hydrogen on Graphene Growth by Plasma-Enhanced Chemical Vapor Deposition

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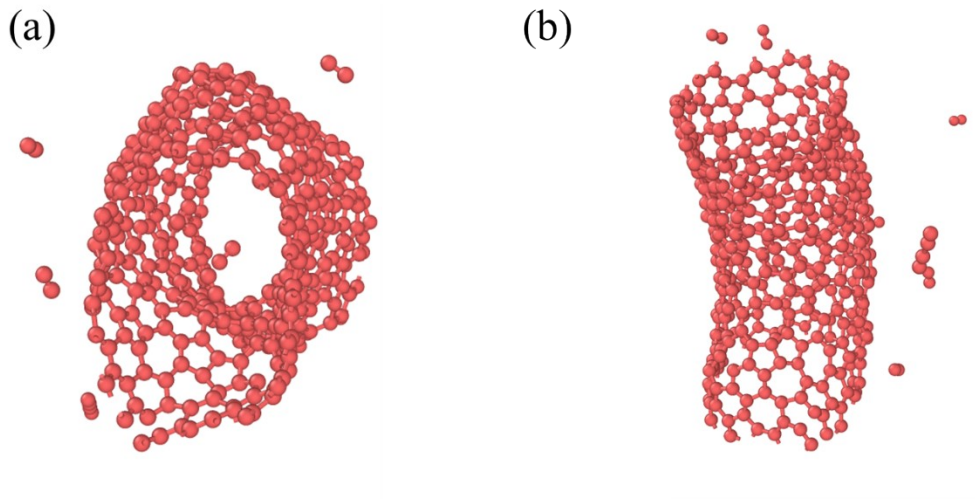

Fig. S1. Snapshots illustrating the tube-like carbon structure in the pure carbon system at 10 ns.

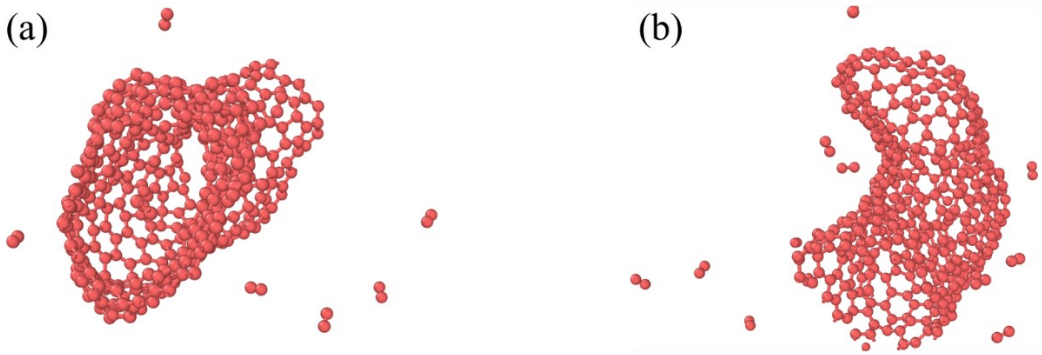

Fig. S2. Snapshots illustrating the tube-like carbon structure in the pure carbon system at 1.2 ns.

Supplementary Section. S1

It is generally accepted that the growth mechanisms of vertically standing graphene nanosheets or nanopetals (GPs) by PECVD involves typically several steps[1,2]: 1) initial stage of nucleation of horizontal graphene sheets parallel to the substrate; 2) crack edges develop and produce nucleation sites for upward curling; and 3) continued accumulation of carbon species resulting in the vertical growth of protruding GPs in the free space. During the third stage, vertically-oriented GPs are growing continuously and steadily into the free space because of the accumulation (i.e., diffusion or direct precipitation) of carbon species at the protruding edges in the plasma environment[1,2]. Here, we conduct RMD simulations to simulate the growth of graphene with a hexagonal carbon ring as the seed and verify the effect of substrates during graphene growth. The results exhibit same trend as that observed in systems without seeds (Figs. S3-6).

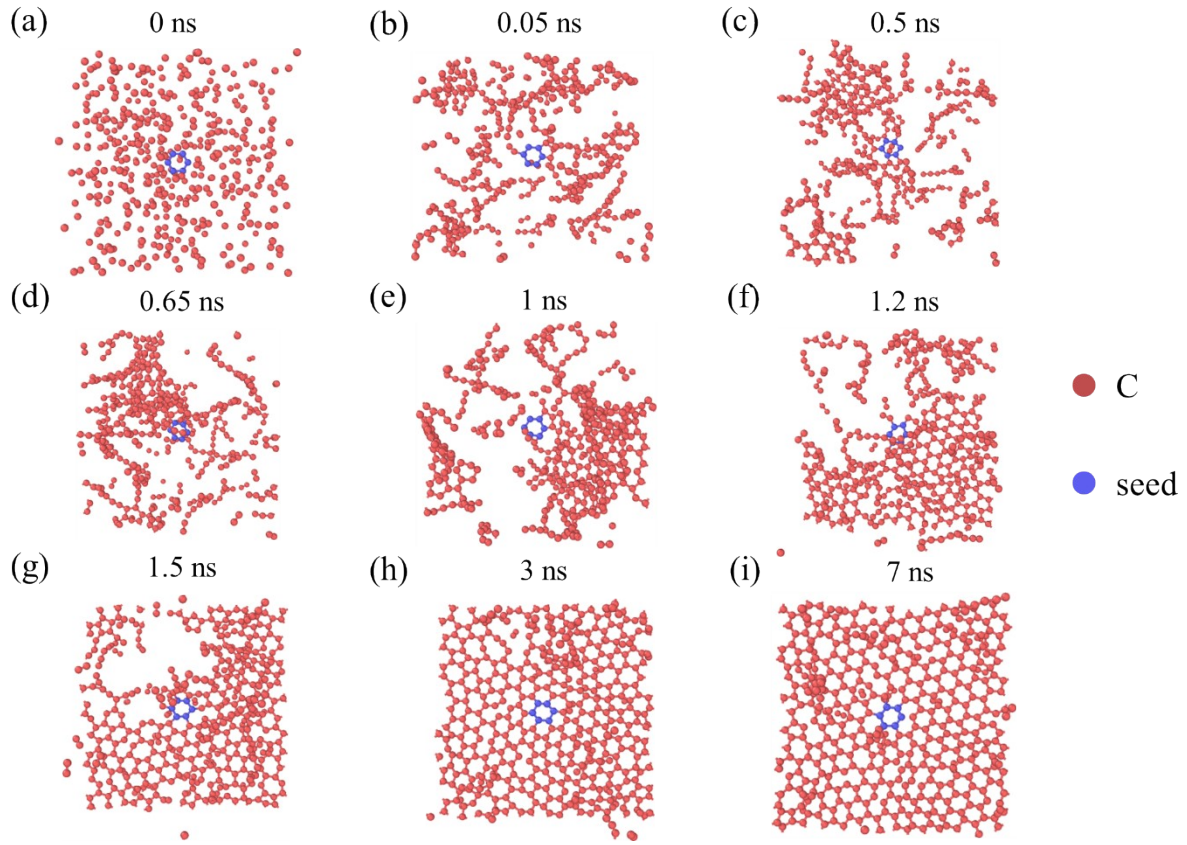

Fig. S3. Snapshots of the formation of graphene network in a system with a C/H ratio of 1:1 when a hexagonal carbon ring is applied as the seed for graphene growth. Red spheres represent carbon atoms. Blue spheres represent the graphene seed. Hydrogen atoms are not shown here for better visualization of the formed carbon structures.

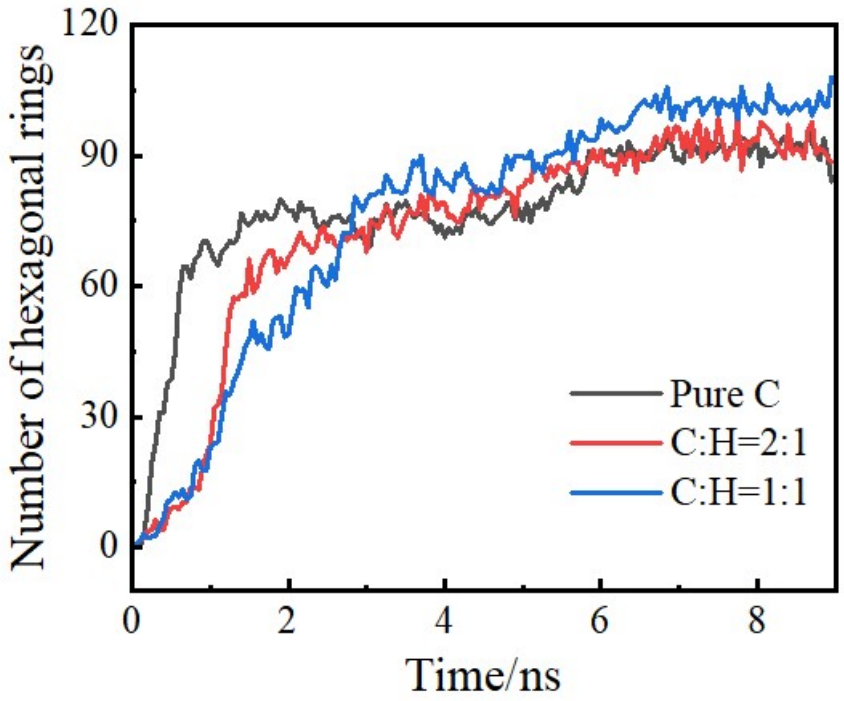

Fig. S4. Number of hexagonal rings as a function of time in the systems with different C/H ratios when a hexagonal carbon ring is applied as the seed for graphene growth. The growth rate of hexagonal carbon rings decreases when the hydrogen content in the precursor increases. In addition, more hexagonal rings are formed in the system with a C/H ratio of 1:1 compared to those formed in the system with a C/H ratio of 2:1 and the pure carbon system.

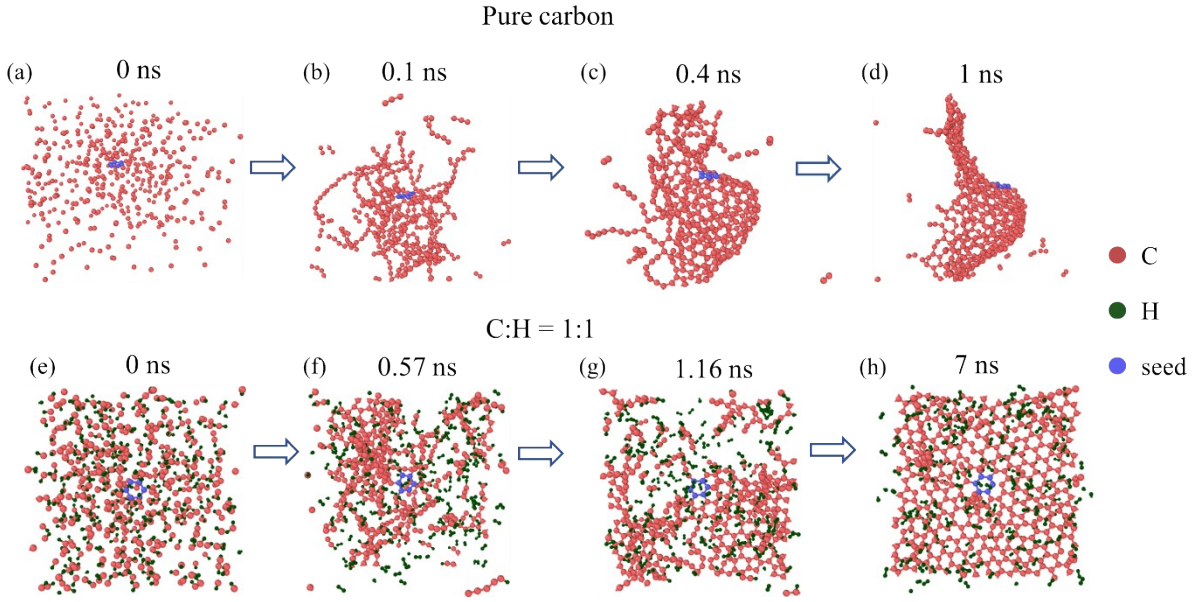

Fig. S5. Structural evolution of a pure carbon system (a) 0 ns, (b) 0.1 ns, (c) 0.4 ns, and (d) 1 ns when a hexagonal carbon ring is applied as the seed for graphene growth. Structural evolution of a system with a C/H ratio of 1:1 (e) 0 ns, (f) 0.57 ns, (g) 1.16 ns, and (h) 7 ns when a hexagonal carbon ring is applied as the seed for graphene growth. Red spheres represent carbon atoms, blue spheres represent the graphene seed, and green spheres represent hydrogen atoms. Notably, increasing the content of hydrogen in the precursors can reduce the growth rate of carbon clusters and prevent the formation of curved carbon structures during the growth process.

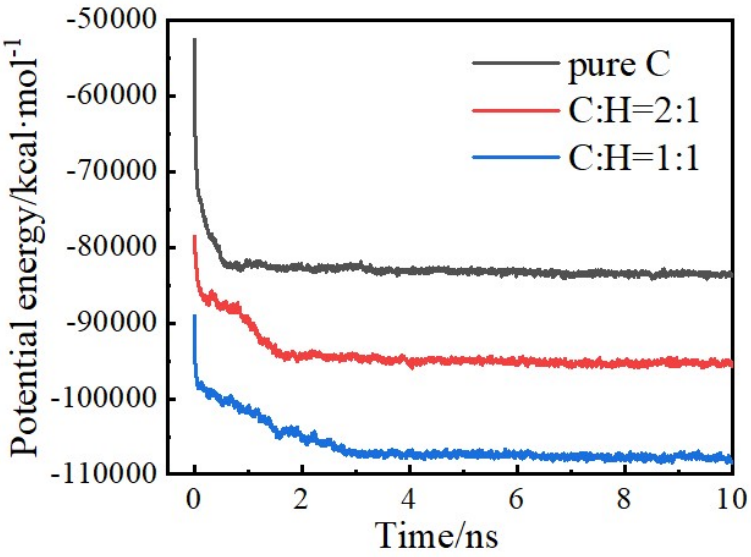

Fig. S6. Comparative potential energies of the systems with different C/H ratios in the precursors as a function of the growth time when a hexagonal carbon ring is applied as the seed for graphene growth.

Supplementary Section. S2

Our simulation results show that the growth rate of graphene decreases significantly in systems with a higher hydrogen content. Although we have calculated for 15 ns (a relatively long simulation time among prior RMD simulations[3–5]), only some long carbon chains are formed within 15 ns in the system with a C/H ratio of 1:2 in the precursors (Fig. S7a). Fig. S8 exhibits the population evaluations of small-size carbon clusters (containing 4-10 carbon atoms), medium-size carbon clusters (containing 11-100 carbon atoms), and large-size carbon clusters (containing more than 100 carbon atoms) as a function of growth time in the system with a C/H ratio of 1:2. The numbers of both small-size and medium-size carbon clusters exhibit negligible changes during 7 ns, which can be attributed to the greatly weakened reactions caused by the high content of hydrogen in the precursor. A large-size carbon cluster is formed around 6 ns and is then dissociated to several smaller carbon clusters. Similar phenomena are observed in the system with a C/H ratio of 1:1 until a stable, large-size carbon cluster is formed. In this case, we can infer that it may take much longer time to obtain stable large-size carbon clusters in the system with a C/H ratio of 1:2.

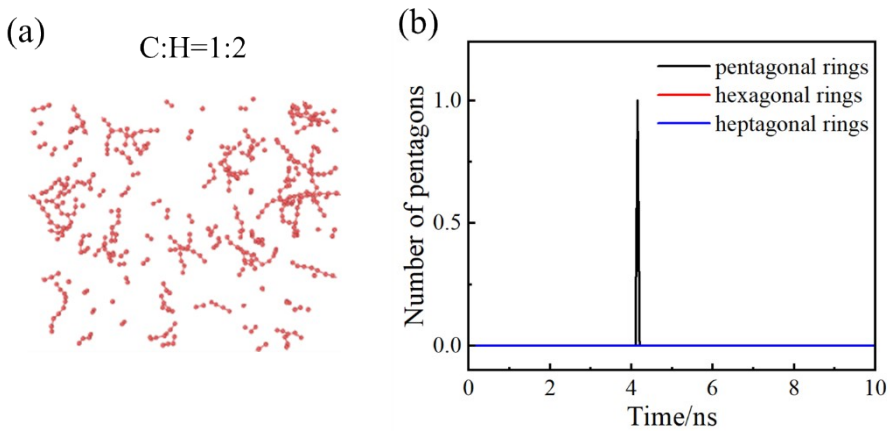

Fig. S7. (a) Snapshots of carbon structures formed in the system with a C/H ratio of 1:2 at 15 ns. Red spheres represent carbon atoms. Hydrogen atoms are not shown here for better visualization of the formed carbon structures. (b) Number of pentagonal, hexagonal, and heptagonal carbon rings as functions of time in a system with a C/H ratio of 1:2.

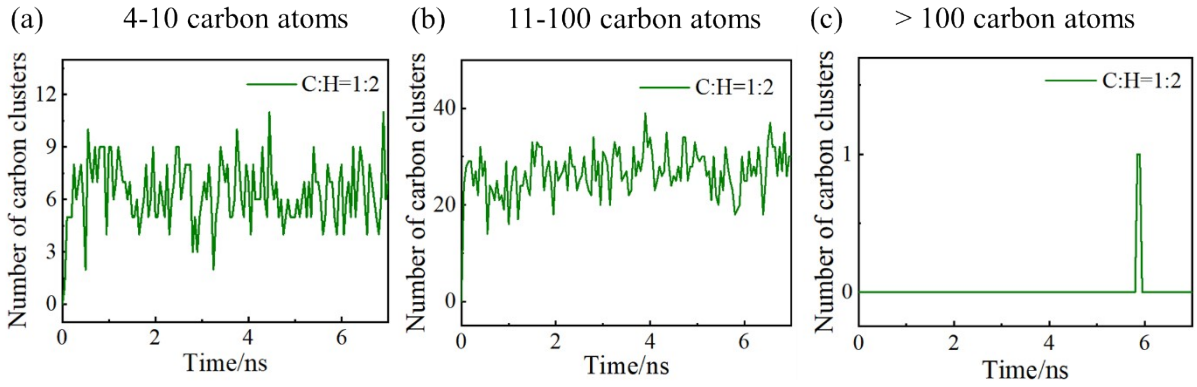

Fig. S8. Number of carbon clusters containing (a) 4-10 carbon atoms; (b) 11-100 carbon atoms; (c) >100 carbon atoms as a function of time in the system with a C/H ratio of 1:2 in the precursors.

References

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