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

Supporting Information

Revealing Reaction Mechanisms of Nanoconfined Li_2S: Implications for Lithium-Sulfur Batteries

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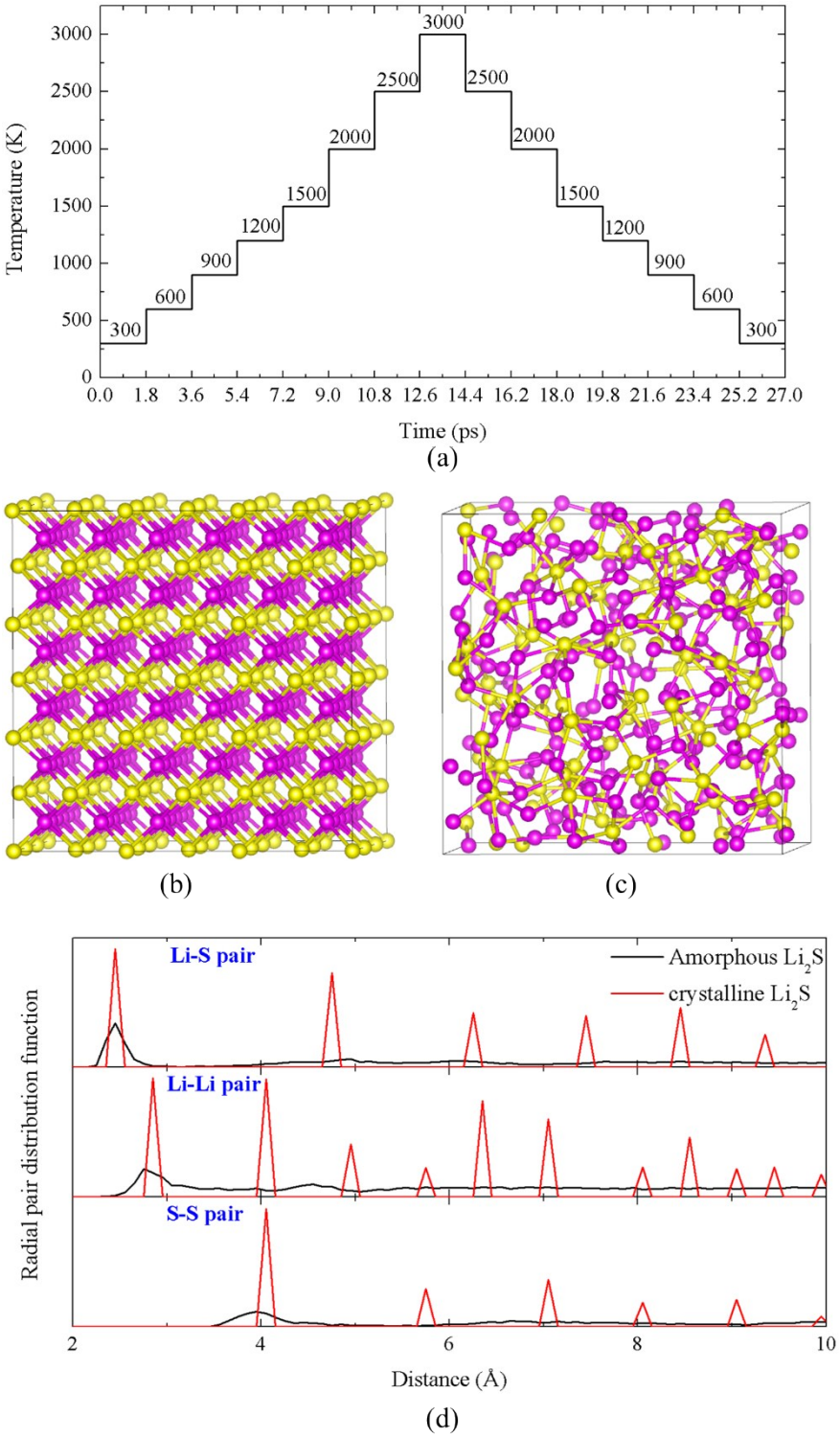

Figure S1. (a) Temperature profile used for melt-and-quench AIMD. (b) Atomistic structure of $(3 \times 3 \times 3)$ crystalline Li_2S supercell. (c) Atomistic structure of amorphous Li_2S. (d) Radial distribution functions of Li-S pair, Li-Li pair and S-S pair in amorphous and crystalline Li_2S.

Figure S1(a) shows the temperature profile during the melt-and-quench

simulation treatment. The time duration at each temperature is 1.8 ps. When the temperature is lower than 1500 K, the AIMD time step is 3 ps, and the time step is decreased to 2 ps when the temperature is higher than 1500 K. After the AIMD simulation, the structure was then optimized by conventional DFT simulation. The melt-and-quench treatment was started from a crystalline Li_2S ($3 \times 3 \times 3$) supercell including 324 atoms as shown in Figure S1(b). Figure S1(c) shows the atomic structure of the amorphous phase after the melt-and-quench treatment. The radial distribution function of Li-S, Li-Li and S-S pairs are plotted in Figure S1(d)

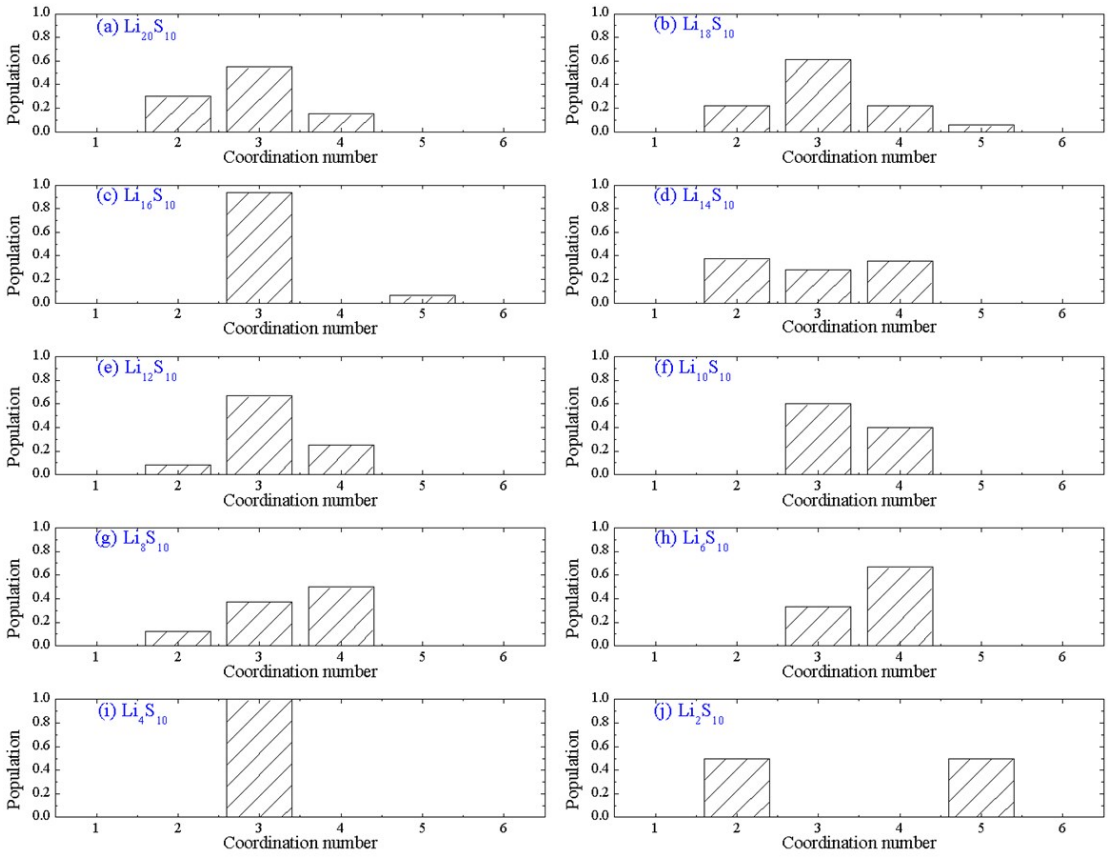

Figure S2. The population of the Li coordination numbers in different Li_xS_{10} clusters.

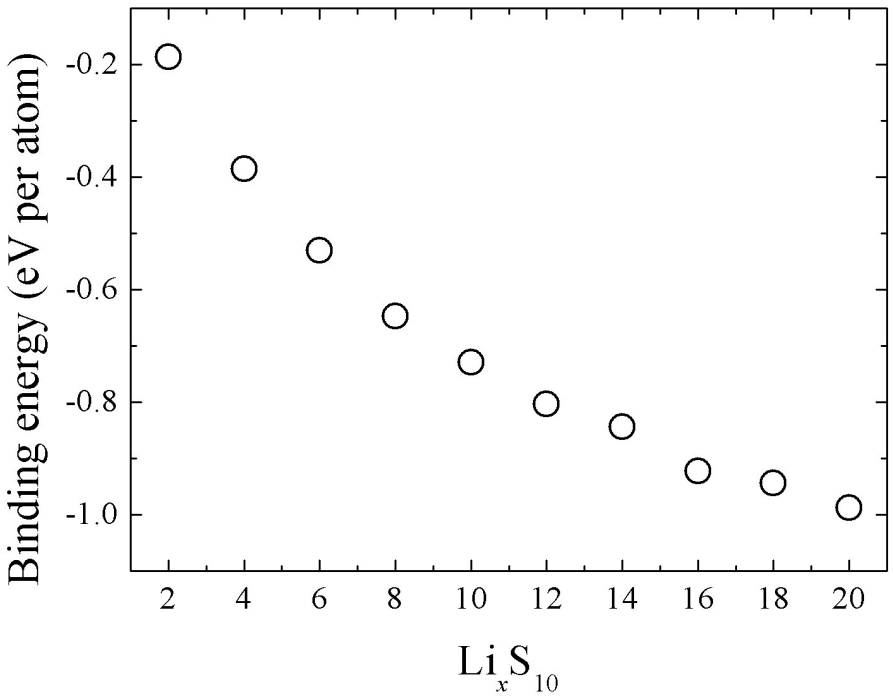

Figure S3. The binding energies of Li_xS_{10} clusters.

The binding energy is calculated as

$$E_b = \frac{E_{Li_xS_{10}} - x \cdot \mu_{Li} - 10 \cdot \mu_S}{x + 10} . \quad \text{(S1)}$$

Here μ_{Li} is the energy per Li atom in the body centered cubic Li crystal, and μ_S is the energy per S atom in the crystalline α-S_8. The negative binding energy indicates that forming a Li_xS_{10} cluster by combining Li atoms and S atoms is thermodynamically favored.

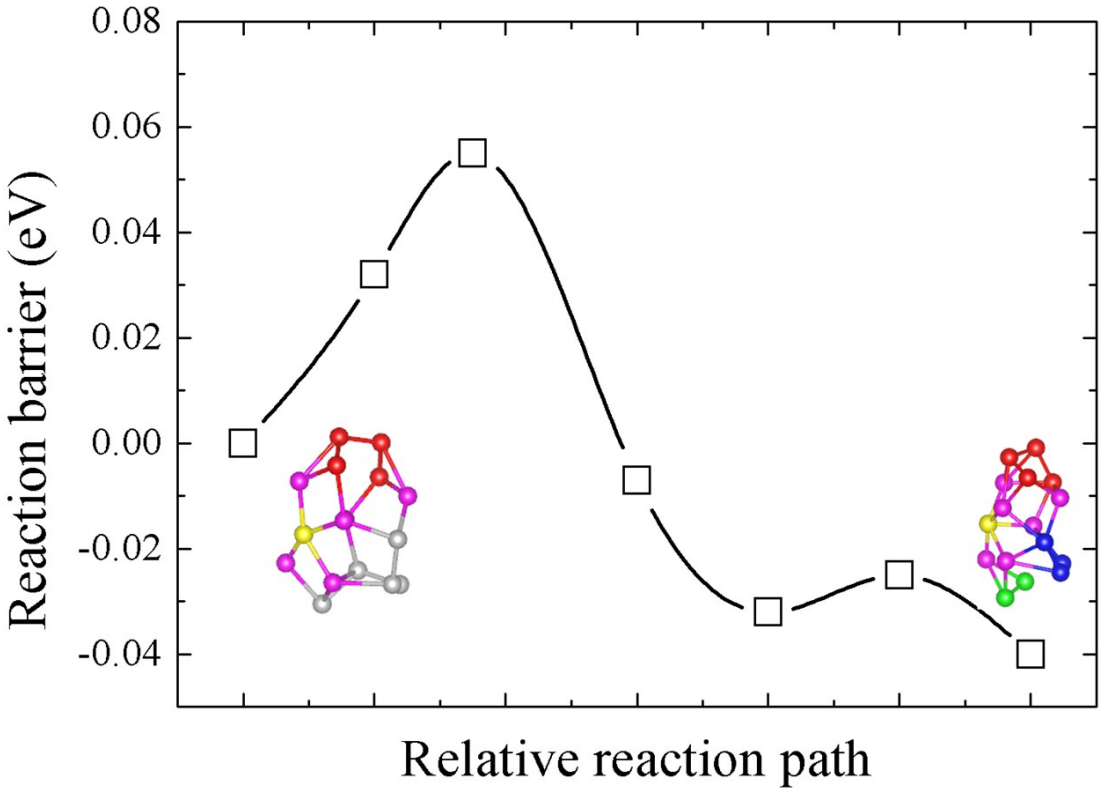

Figure S4. The reaction barrier of S_5^{2-} disproportionation to S_2^- and S_3^- in the Li_6S_{10} cluster. The initial state was adapted from the AIMD simulation at 1 ps, and the final state was adapted from the AIMD simulation at 2ps. The minimum energy barrier was searched using the climbing image nudge elastic band method.[1]

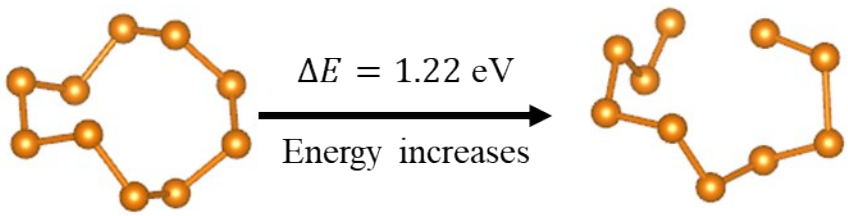

Figure S5. Opening the cyclo-S_{10} ring is an endothermic process with an energy increase of 1.22 eV.

References

(1) Henkelman, G.; Uberuaga, B. P.; Jonsson, H. *Journal of Chemical Physics* **2000**, *113*, 9901.