

## ELECTRONIC SUPPLEMENTARY MATERIALS

# Excited State Dynamics Study of the Self-Trapped Exciton Formation in Silicon Nanosheets

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### **Discussion on the Reliability and Accuracy of TD-DFTB Method**

In the present study, we have used the DFTB adiabatic dynamics, where at each time step, the DFTB calculations carried out; tracing out the electronic structure at each time step. In adiabatic dynamics, the Born-Oppenheimer approximation is validated at each step with slowly varying nuclear co-ordinates to avoiding any crossing of the surfaces. At the point of crossing, the Born-Oppenheimer approximation breaks down (the calculations will stop) and the nuclei may ignore the small gap of avoided crossing adopting the new configuration which is typical of non-adiabatic behavior [1]. DFTB adiabatic dynamics, every time step generates the results for the ground- and excited-states to make sure that the dynamics run on the correct state, that is, S1 state.

Recently, the TD-DFTB combined with FSSH technique shown reliability and capability of handling accurately the non-adiabatic excitation dynamics of CdSe quantum dot and semiconducting carbon nanotube on expanse of the modest computational cost tested against the expensive ab-initio DFT and experimental data. [2]

Regarding the reliability of DFTB method, many studies have shown the accuracy of DFTB method and found that it can make a good balance between accuracy and computational cost. Recently, demand for the large scale calculations persuades because of the TD-DFT simulations are limited to about hundred atoms systems. Self-consistent charge density functional tight binding (SCC-DFTB) method is capable of increasing the system size by an order of magnitude. Parameterized against the DFT, the SCC-DFTB provides a quantum mechanical description of the geometries, vibrational frequencies, reaction energies and other properties of very large systems

at the modest computational cost. [3-7] Similarly, recent TD-DFTB excited state dynamics study prove it to be a reliable and capable method, handling accurately the excitation dynamics of large scale materials assessed against the expensive ab-initio DFT and experimental data. [2] Also, the DFTB methodology well described the quantum plasmonics and offers a firm basis to overcome the bottleneck of computational cost in plasmonics and paves the way toward future developments in quantum plasmonics. [8,9]

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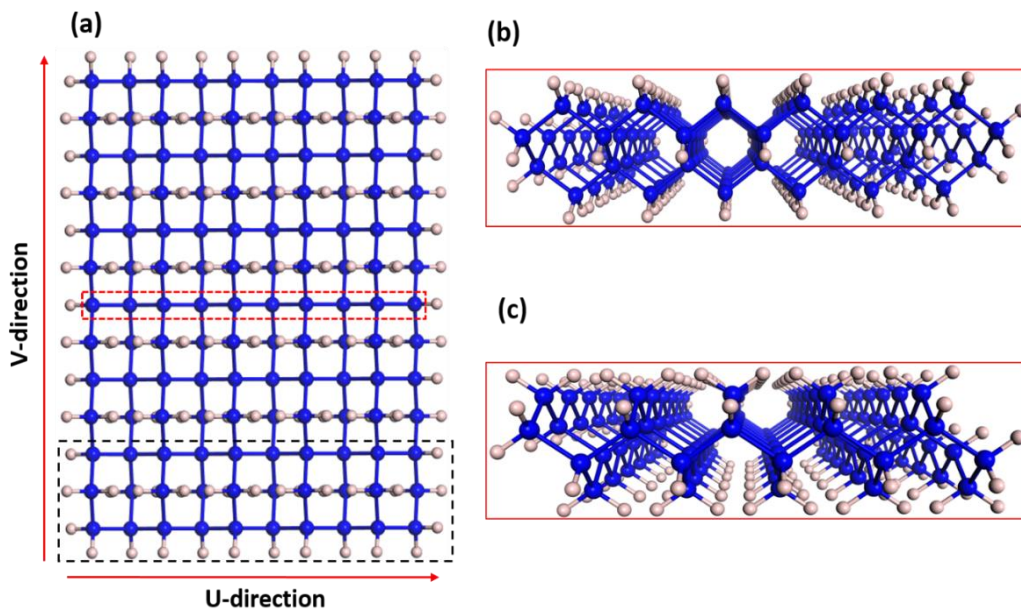


Figure S1: Silicon nanosheets (SiNSs) (a) The size of the NSs initiated from a fixed length (U-direction) and expanded via increase in the width (V-direction). The initial structure is shown by a dashed line (black) while a dashed red colored line indicates the symmetrical Si-Si bond layer. (b) Side view of the SiNS in U direction (c) Side view of the SiNS in V direction.

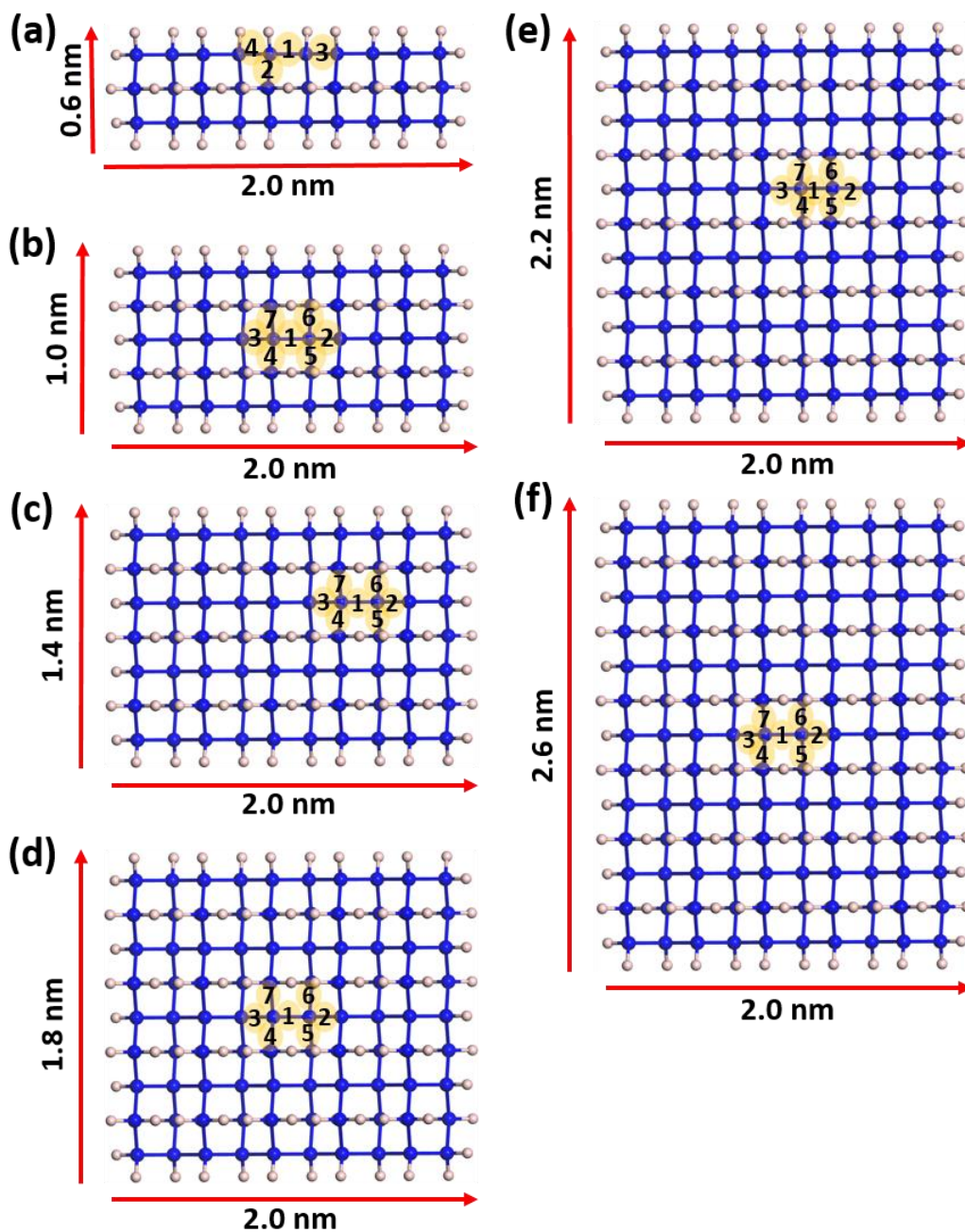


Figure S2: Si NSs of different length\*width ( $U \times V$ ) comprising of  $U=2.0$  and increasing width i.e. (a)  $V=0.6$ , (b)  $V=1.0$ , (c)  $V=1.4$ , (d)  $V=1.8$ , (e)  $V=2.2$ , (f)  $V=2.6$ , where  $U$  and  $V$  values are in nanometer. The numbered bonds are indicative of the sensitive sites for exciton trapping.

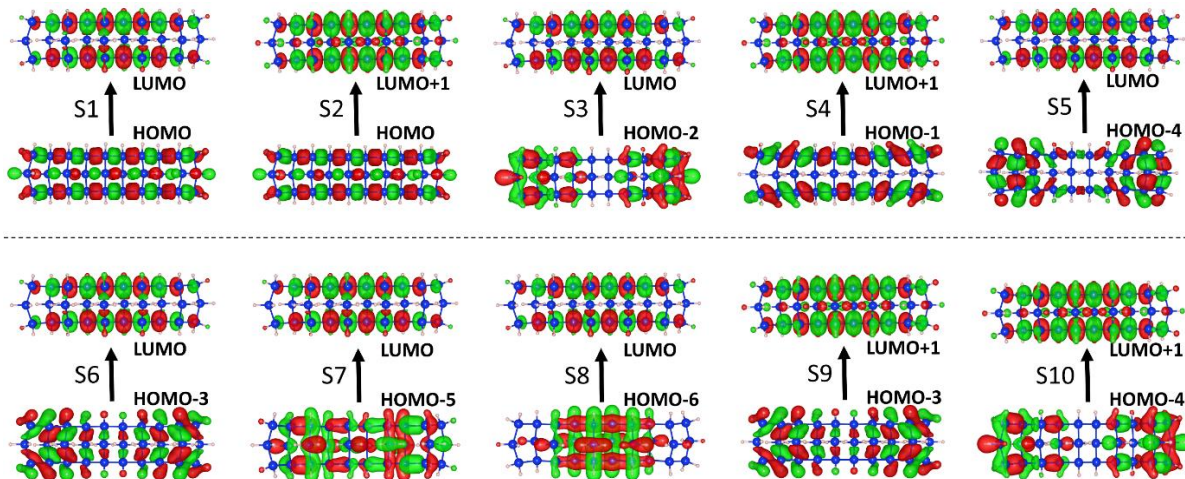


Figure S3: The representative pairs of transition-orbitals for first ten excitations in Si(0.6).

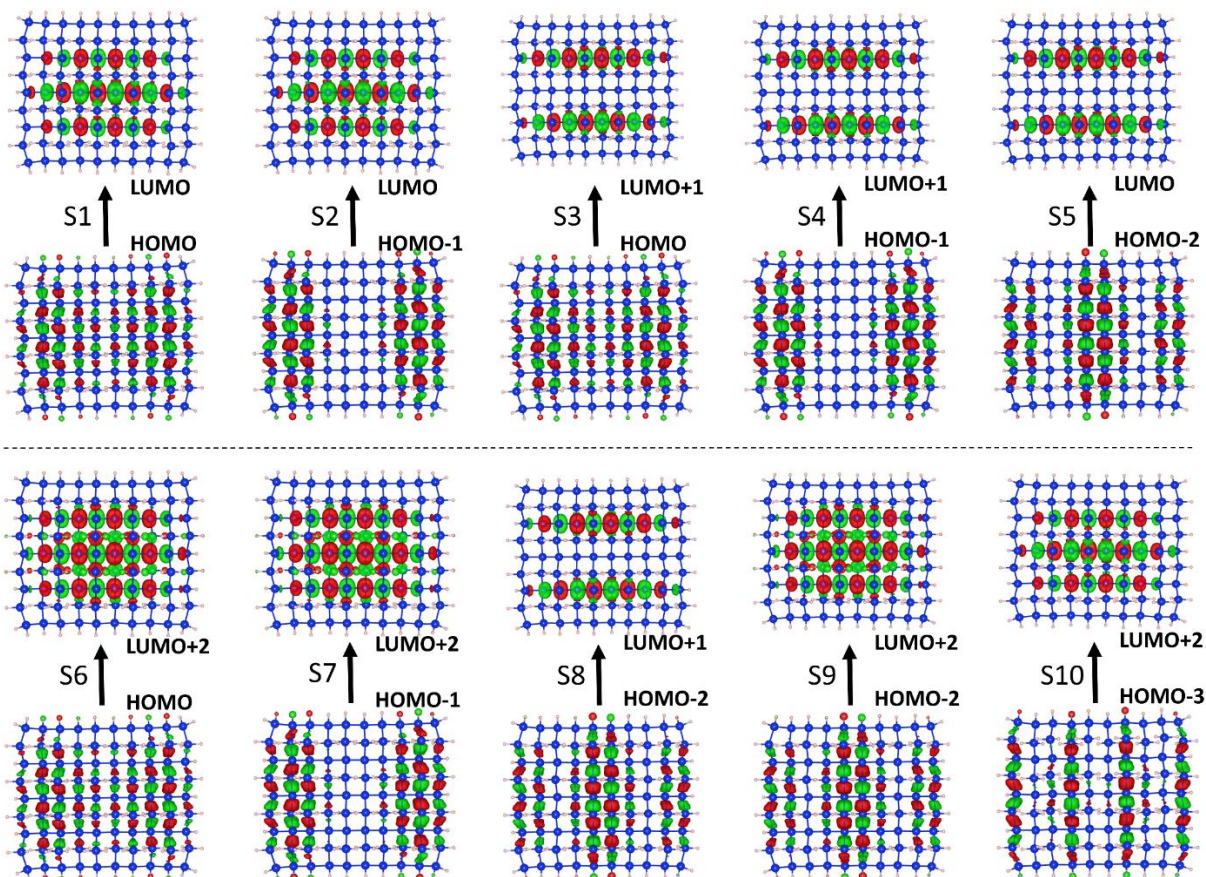


Figure S4: The representative pairs of transition-orbitals for first ten excitations in Si(1.8).

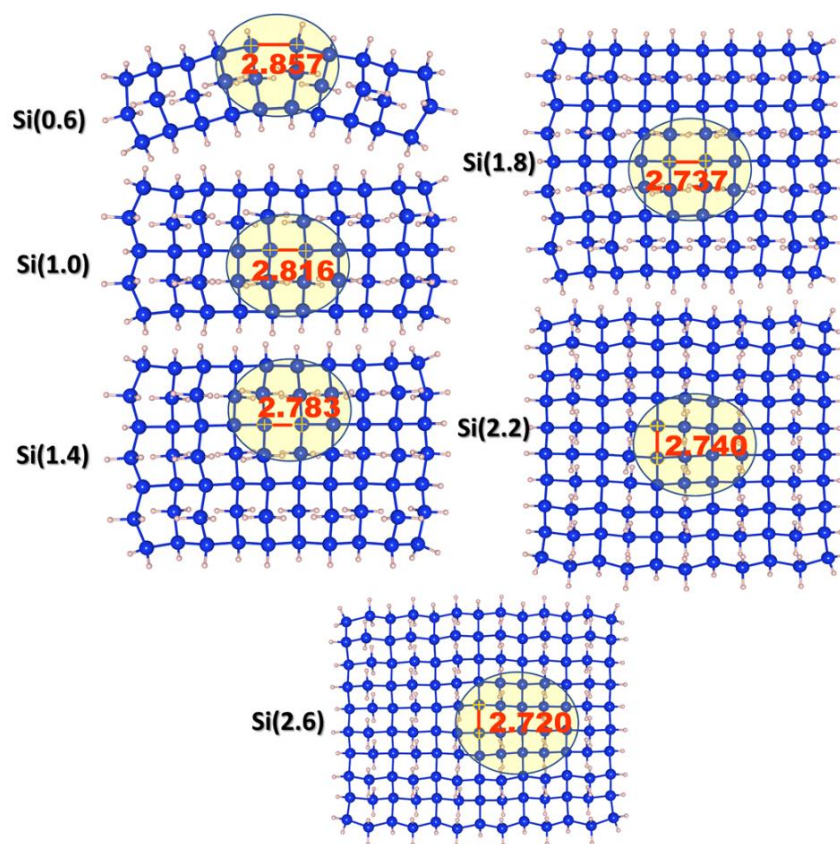


Figure S5: The optimized S1 structures for all SiNSs with the highlighted broken bonds and their bond lengths are given. Red line and numerical value indicate the broken bond and distance between the two atoms respectively.

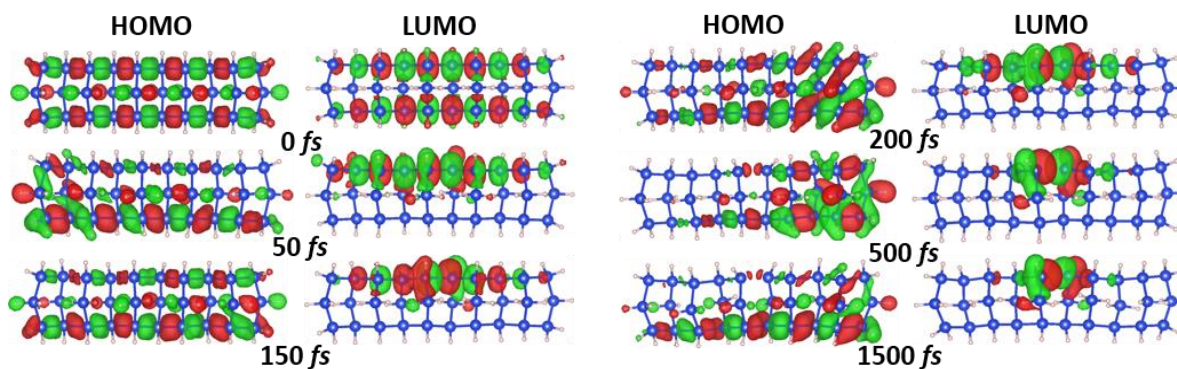


Figure S6: The time evolution of the excited state (S1) frontier orbital structure for Si(0.6) NS.

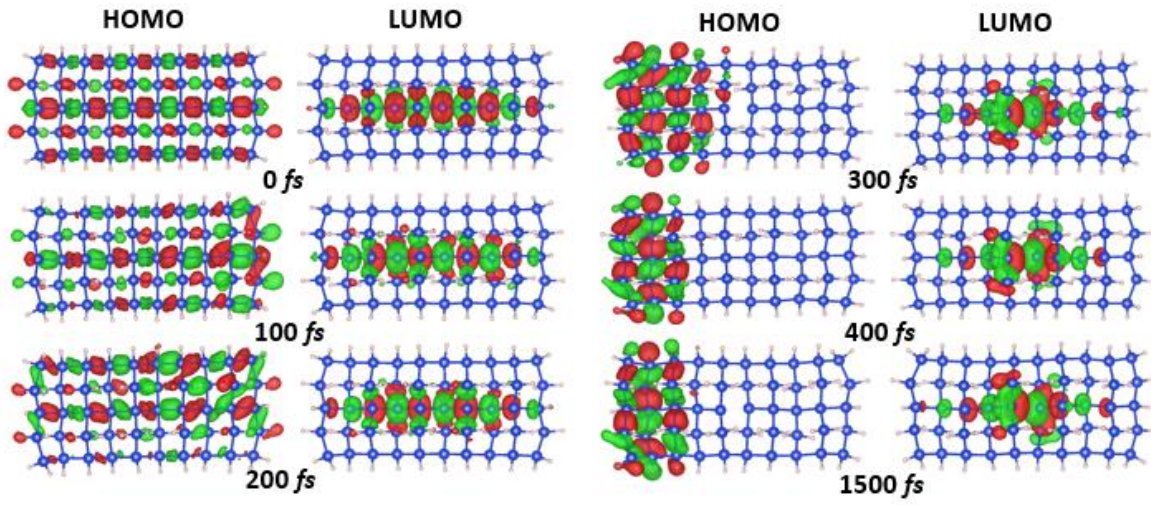


Figure S7: The time evolution of the excited state (S1) frontier orbital structure for Si(1.0) NS.

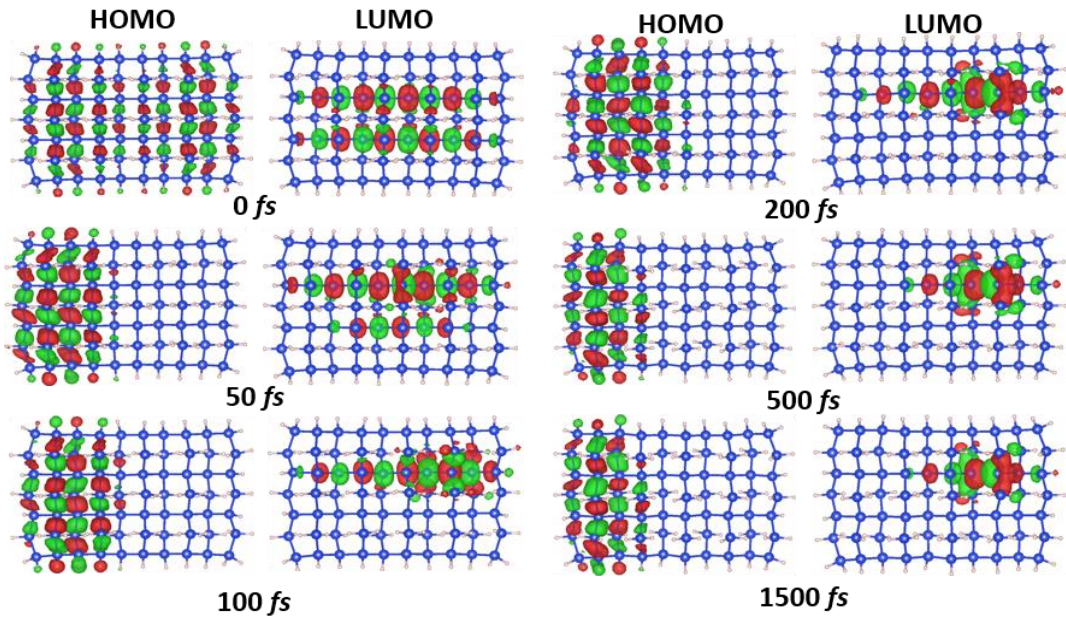


Figure S8: The time evolution of the excited state (S1) frontier orbital structure for Si(1.4) NS.

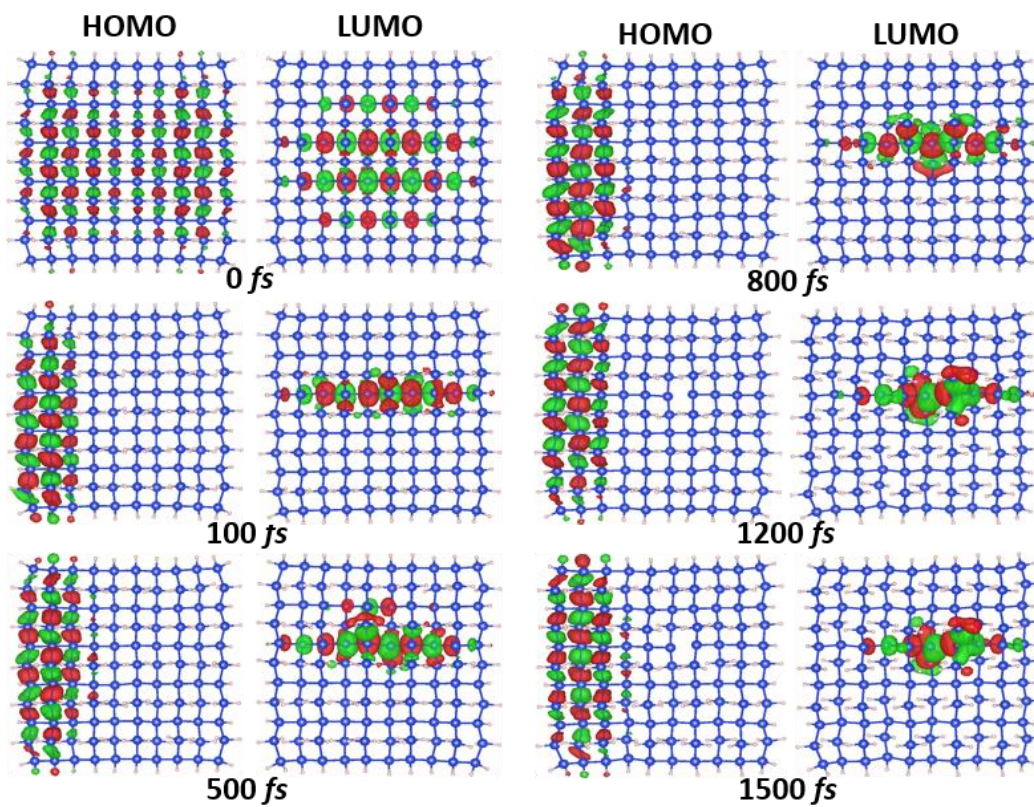


Figure S9: The time evolution of the excited state (S1) frontier orbital structure for Si(2.2) NS.



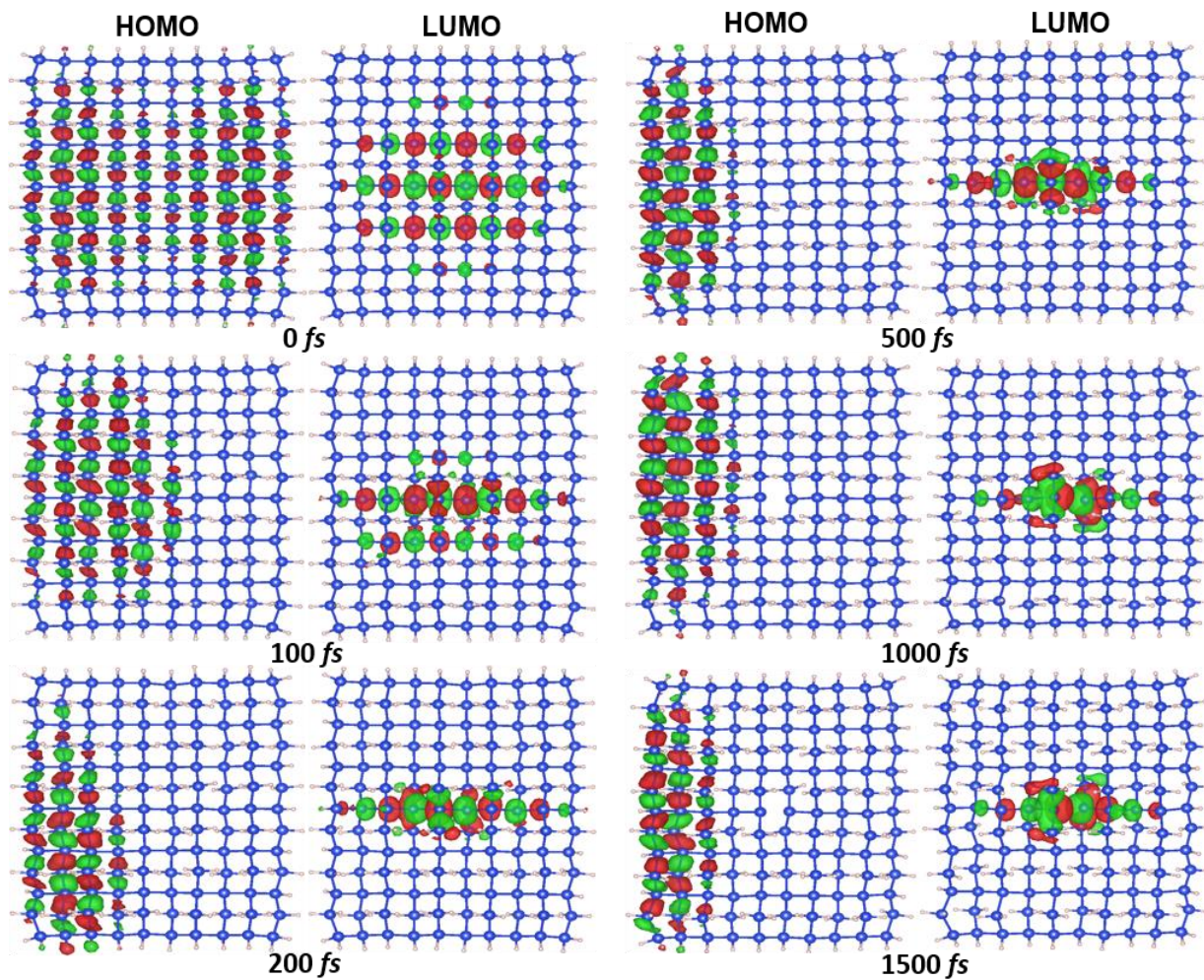


Figure S10: The time evolution of the excited state (S1) frontier orbital structure for Si(2.6) NS.

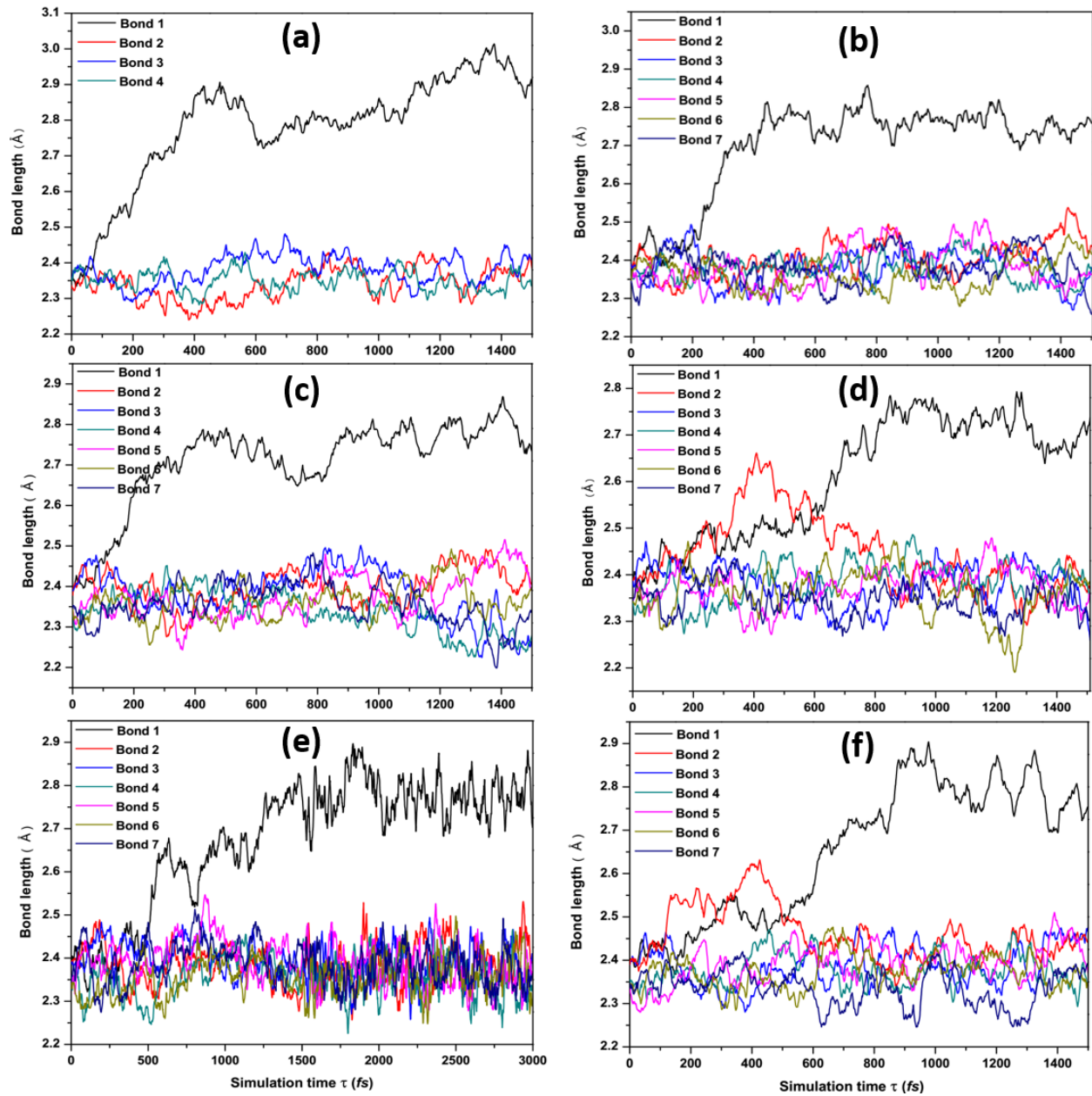


Figure S11: Time evolution of the bond length trajectories for (a) Si(0.6), (b) Si(1.0), (c) Si(1.4), (d) Si(1.8), (e) Si(2.2) and (f) Si(2.6). The relevant bonds are designated in the Figure S2.

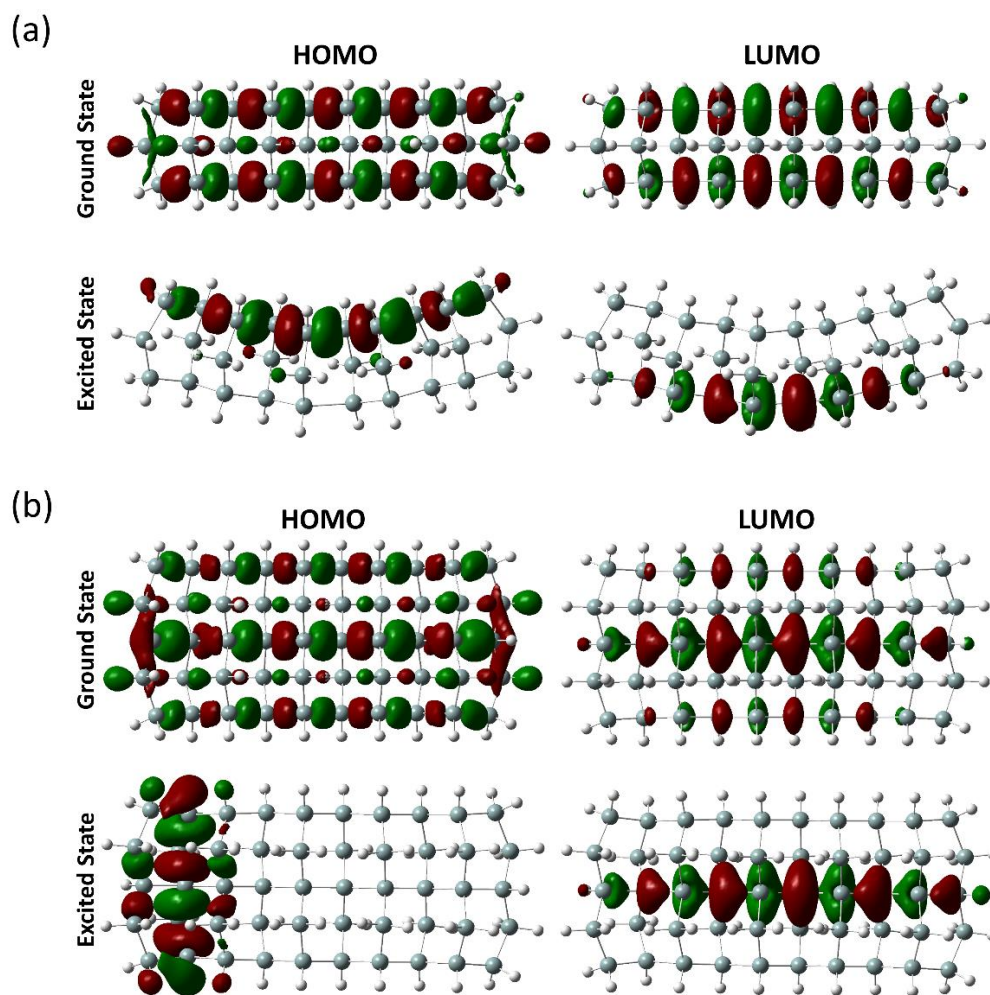


Figure S12: Excited-state frontier orbitals display for (a) Si(0.6) (b) Si(1.0) nanosheets obtained at TD-DFT CAM-B3LYP/6-31G(d) level. Comparison with the TD-DFTB orbitals results in Figure 2 shows satisfactory agreement.

Table S1. Absorption energies with oscillator strength for first ten transitions for Si(0.6).

Transition No.	E (eV)	$f(a.u)$
1	4.511	0.0007011
2	4.561	0.0197884
3	4.694	0.0000268
4	4.698	0
5	4.707	0.5297689
6	4.708	0
7	4.778	0.0000166
8	4.792	0
9	4.794	0.0033758
10	4.803	0

Table S2. Absorption energies with oscillator strength for first ten transitions for Si(1.0).

Transition No.	E (eV)	$f(a.u)$
1	3.921	0.0000125
2	3.961	0.1307942
3	3.962	0.008918
4	4.022	0.0021476
5	4.041	0
6	4.07	0
7	4.117	0
8	4.133	0.0017437
9	4.187	0.0102159
10	4.209	0

Table S3. Absorption energies with oscillator strength for first ten transitions for Si(1.4).

Transition No.	E (eV)	$f(a.u)$
1	3.76	0.0000028
2	3.796	0.0005558
3	3.863	0.0246537
4	3.869	0
5	3.881	0
6	3.924	0
7	3.931	0.0035631
8	3.948	0.0001968
9	3.95	0.0254693
10	3.998	0.0000016

Table S4. Absorption energies with oscillator strength for first ten transitions for Si(1.8).

Transition No.	E (eV)	$f(a.u)$
1	3.551	0.0004117
2	3.563	0
3	3.62	0
4	3.632	0.0004317
5	3.655	0.0004335
6	3.658	0.0456474
7	3.666	0
8	3.723	0
9	3.756	0.0055166
10	3.763	0

Table S5. Absorption energies with oscillator strength for first ten transitions for Si(2.2).

Transition No.	E (eV)	$f(a.u)$
1	3.481	0.0000024
2	3.496	0.0000164
3	3.523	0.0005854
4	3.536	0
5	3.574	0
6	3.575	0
7	3.587	0.073773
8	3.587	0.0003696
9	3.595	0
10	3.628	0.0000986

Table S6. Absorption energies with oscillator strength for first ten transitions for Si(2.6).

Transition No.	E (eV)	$f(a.u)$
1	3.416	0.000089
2	3.428	0
3	3.458	0
4	3.471	0.0000106
5	3.505	0.0002595
6	3.518	0
7	3.522	0.0000097
8	3.537	0.1074411
9	3.541	0
10	3.545	0