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Supporting Information

Theoretical investigation of growth, stability, and electronic properties of beaded ZnO nanowires

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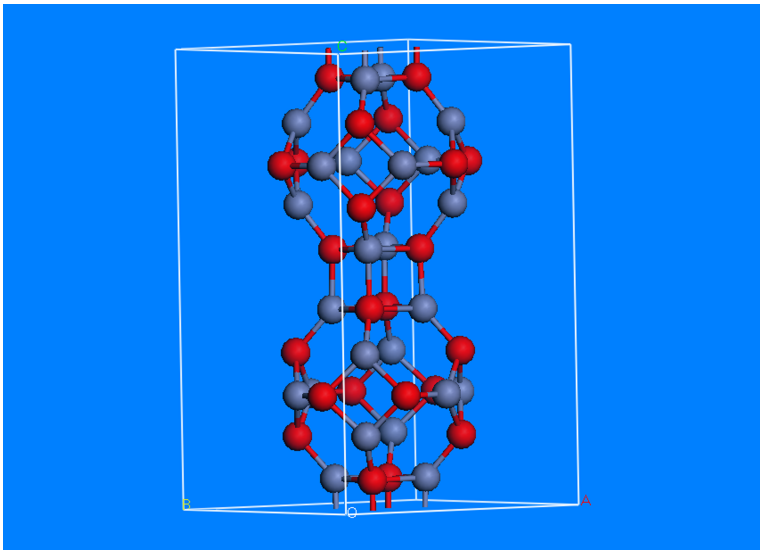
S1. Lattice constants

The optimized ZnO clusters are put into orthorhombic supercells, which are large enough to be able to ignore the interaction between each structure and its periodic images. The nearest distance between two neighbor clusters is about 15 Å. In order to give a clear technical detail, all the lattice constants are shown. (In the following data, a_L, b_L, and c_L are the length of the $(ZnO)_{12\times n}$ cluster; a, b, and c are the lattice constants.)

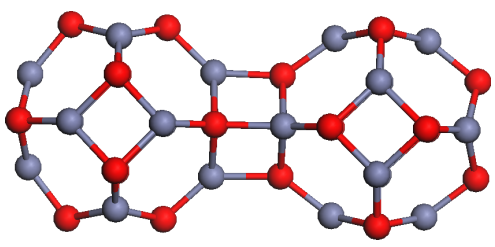
$(ZnO)_{12}$	$a_L = b_L = c_L$ = 5. 57 Å	Supercell: a = b = 20.57 Å, c = 20.57 Å
$(ZnO)_{12\times2}$	c_L = 13.15 Å	Supercell: a = b = 20.57 Å, c = 28.15 Å
$(ZnO)_{12\times3}$	c_L = 21.16 Å	Supercell: a = b = 20.57 Å, c = 36.16 Å
$(ZnO)_{12\times4}$	c_L = 28.58 Å	Supercell: a = b = 20.57 Å, c = 43.58 Å
$(ZnO)_{12\times5}$	c_L = 36.59 Å	Supercell: a = b = 20.57 Å, c = 51.59 Å
$(ZnO)_{12\times6}$	c_L = 43.95 Å	Supercell: a = b = 20.57 Å, c = 58.95 Å

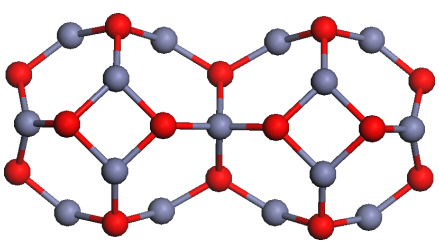
On the other hand, we have calculated an infinite ZnO nanostructure, as shown in the following figure. The optimized lattice constants of dimmer ZnO have been listed, a = 9.518 Å, b = 9.456 Å, c = 15.377 Å.

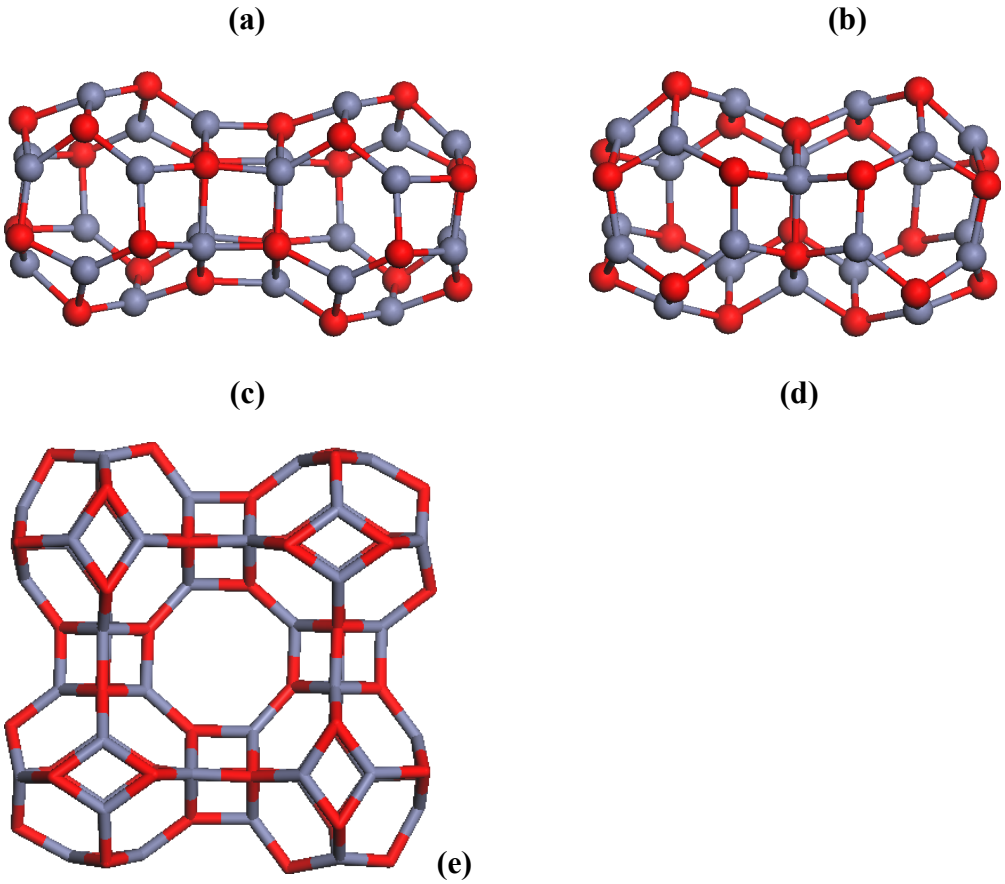


S2. Four models

In fact, there are four models in the following figure(a-d), can be constructed by conneting or sharing $(ZnO)_2$ and $(ZnO)_3$ facets. Our calculation shows that the binding energies of four models from figure (a) to figure (d) are 76.74, 69.64, 76.83, 76.85 eV, respectively. From the results, the models (a), (c) and (d) have nearly equal value, which are more stable with large binding energies than model (b). In addition, we choose the model (a) with $(ZnO)_2$ facets because zeolite-shaped ZnO have also similar connection by $(ZnO)_2$ facets, which can be seen in figure (e). One can find that a regular cluster can be easily formed by connecting $(ZnO)_2$ facets.







S3. Zero point energy

Zero point energy (ZPE) of ZnO clusters: (1.00 Ha = 627.51 kcal/mol)

$(ZnO)_{12}$ 28.34 kcal/mol

$(ZnO)_{12\times2}$ 57.30 kcal/mol

$(ZnO)_{12\times3}$ 86.21 kcal/mol

$(ZnO)_{12\times4}$ 115.06 kcal/mol

$(ZnO)_{12\times5}$ 144.11 kcal/mol

$(ZnO)_{12\times6}$ 172.68 kcal/mol

S4. Energy gain $E(n)$

We have calculated the energy gain $E(n)$ by systematically assembling one $(ZnO)_{12}$ unit at a time as the beaded ZnO nanowire grows.

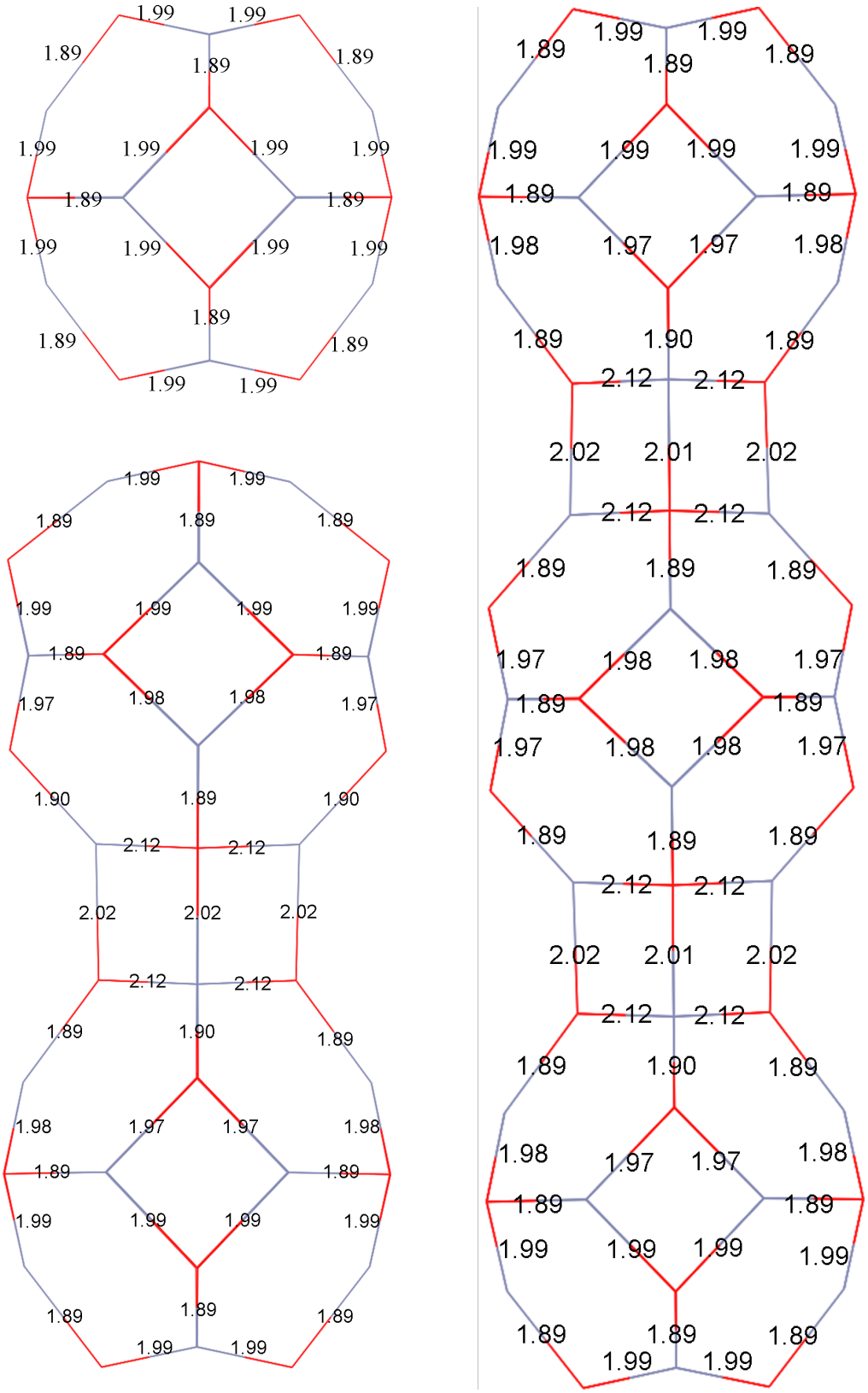
$$E(n) = E(ZnO)_{12\times(n-1)} + E(ZnO)_{12} - E(ZnO)_{12\times n}$$

The major contribution of this energy would be given by the four Zn-O bonds formed so it may be interesting to follow how these bond energies change during the wire growth.

E(2) = 2.360 eV, *E(3)* = 2.361 eV, *E(4)* = 2.319 eV, *E(5)* = 2.335 eV

From the calculated result, we can estimate the strength of every created bond. The bond energies of the Zn-O bonds in nanocontact have no significant changes, and only the $(ZnO)_{12\times4}$ have slightly large bond energy, 2.361 eV, than others. Besides, we have also calculated the average strength of the bonds inside the $(ZnO)_{12}$ cluster. The average bond energy of the $(ZnO)_{12}$ cluster is 2.357 eV.

Fig. S1. The Zn–O bond lengths of the optimized $(ZnO)_{12}$ cluster and beaded ZnO nanowires. The red and gray balls represent O and Zn atoms.



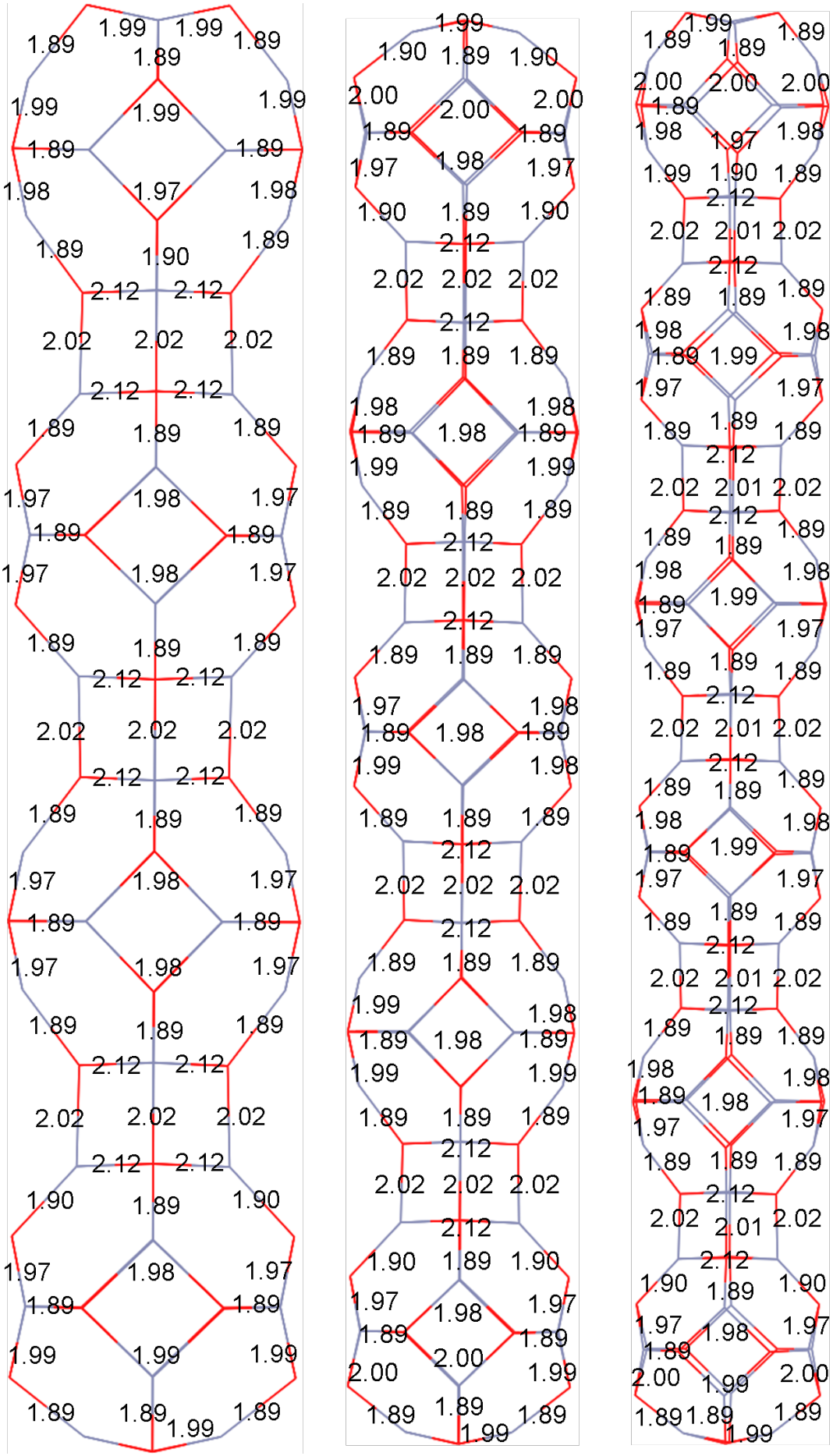
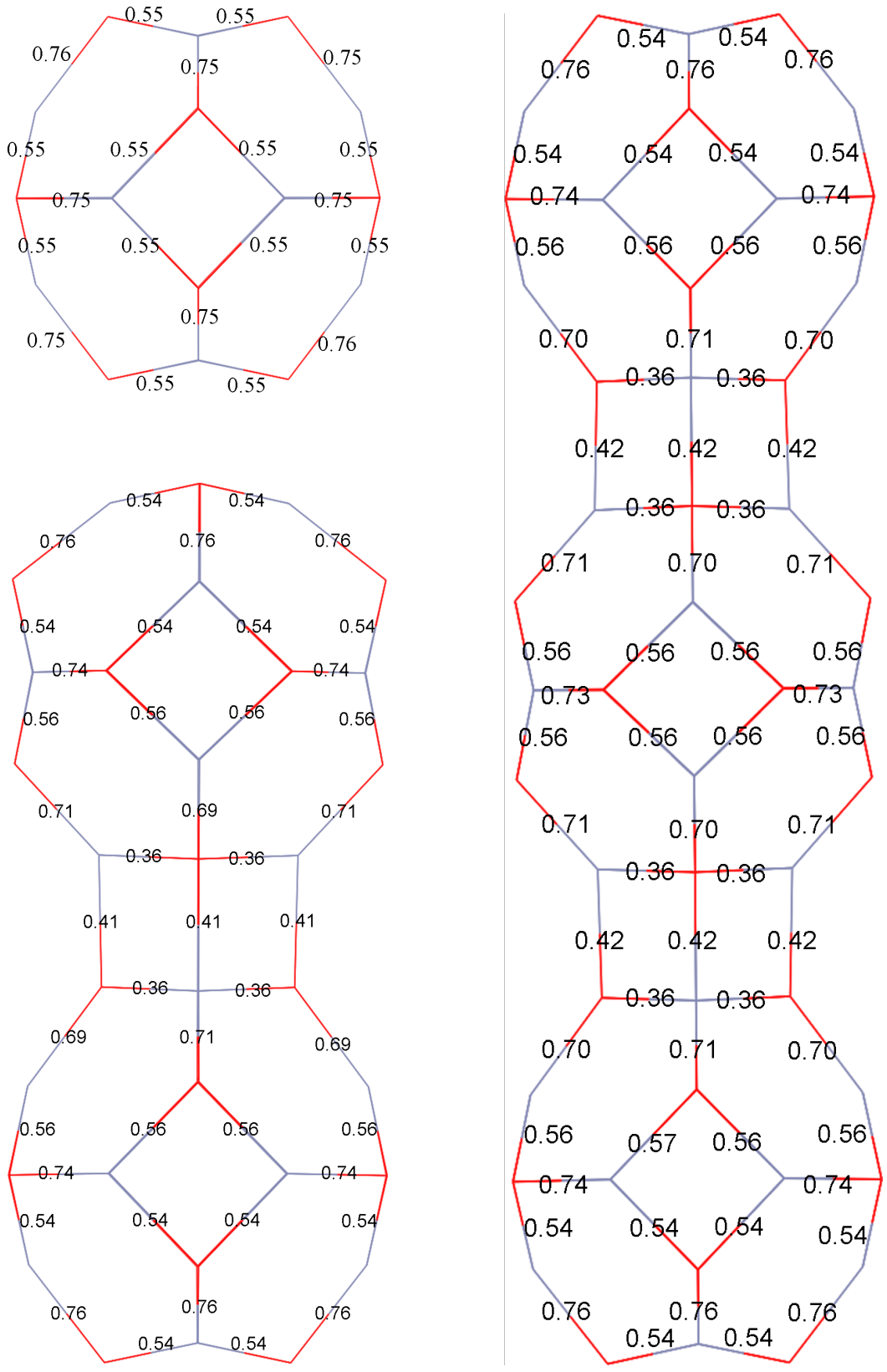


Fig. S2. Mayer bond orders of the optimized $(ZnO)_{12}$ cluster and beaded ZnO nanowires. The red and gray balls represent O and Zn atoms.



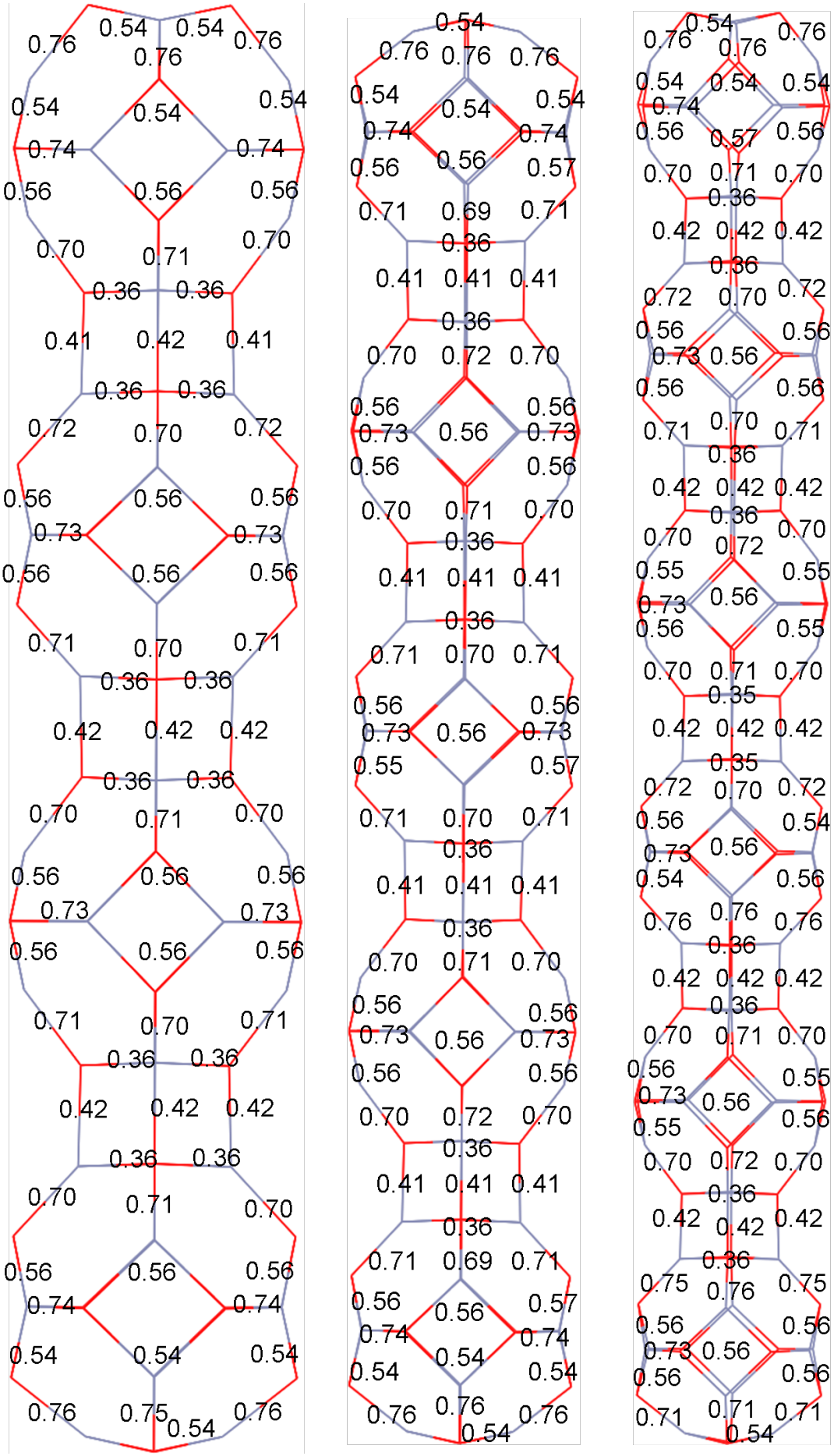


Fig. S3. Slices of deformation electronic density through the ZnO nanowire axis. The red and gray balls represent O and Zn atoms.

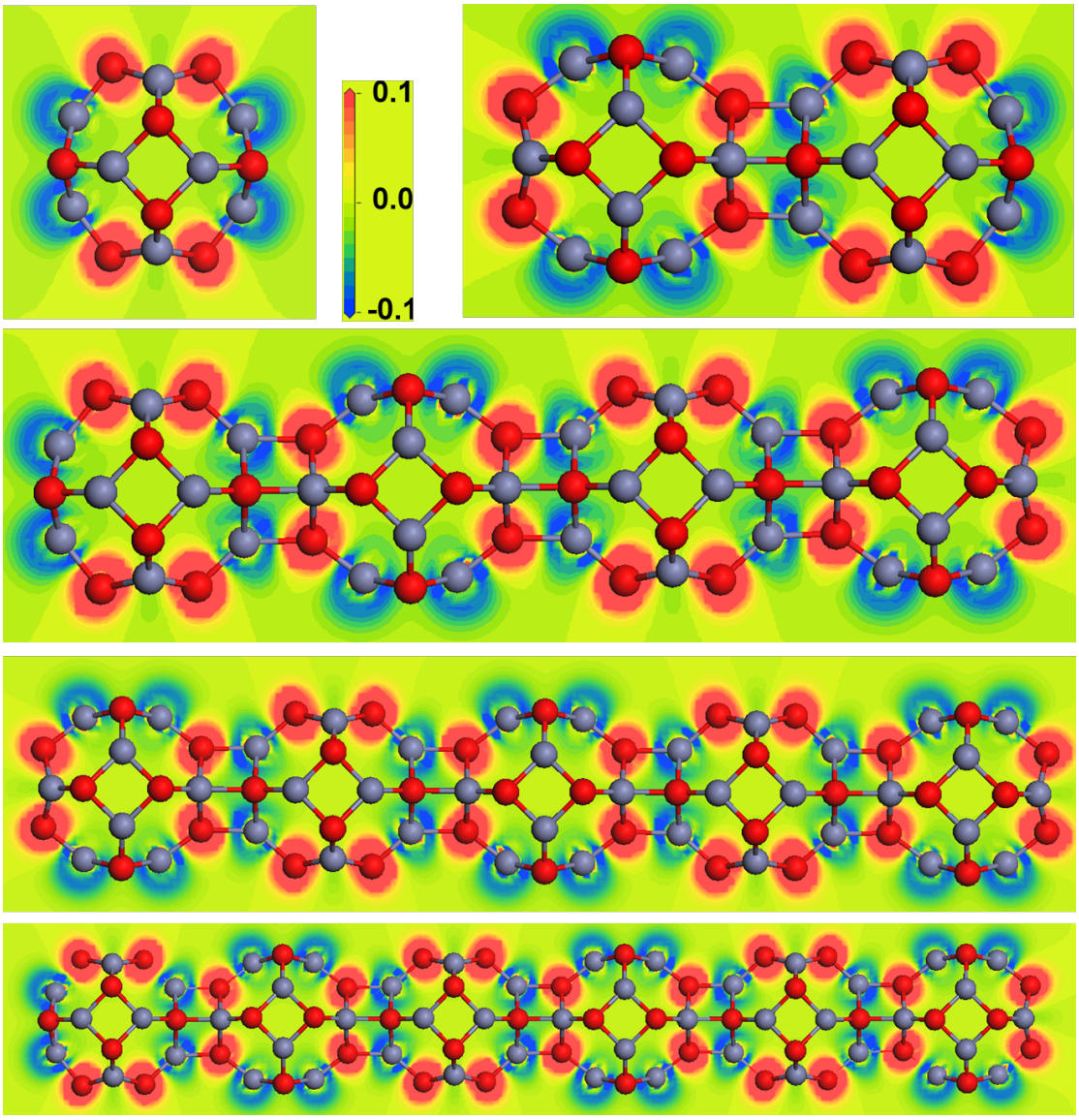


Fig. S4. Vibrational spectra of the beaded $(ZnO)_{12\times5}$ nanowire. The red and gray balls represent O and Zn atoms.