## Supplementary Information

Oxygen vacancy mediated cubic phase stabilization at room temperature in pure nano-crystalline Zirconia films: A combined experimental and first-principles based investigation

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PCF (or Radial Distribution Function) of a 1 nm cubic cluster and 10 nm cubic cluster
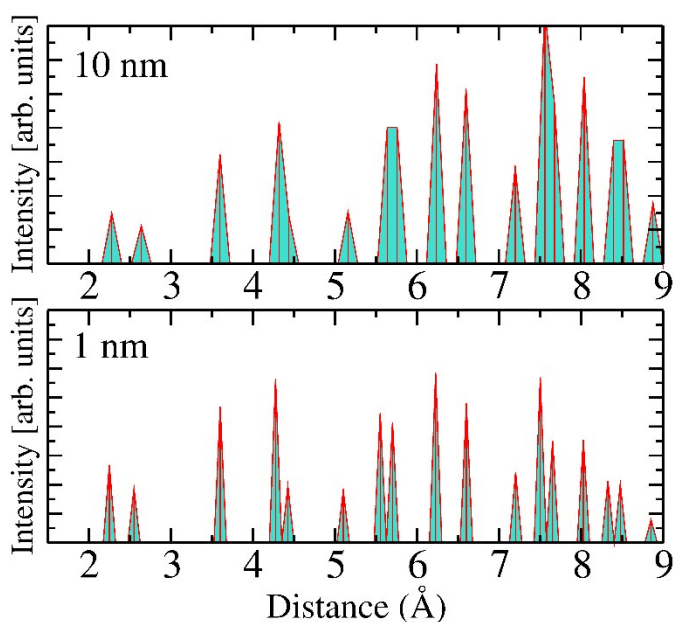
Figure S1: PCF of 1 nm and 10 nm clusters.

Note that, the PCF is calculated by estimating all possible bond-lengths of the clusters and thereby splitting them into equi-spaced bins. This takes into account the numbers of neighboring atoms at particular distances i.e. how many atoms are there within the first co-ordination shell, how many are there in the second co-ordination shell etc.

Photoluminescence (PL) spectra of S3 film

The PL measurements were performed in order to validate that the S3 film is indeed having charged oxygen vacancies (as predicted from our simulation results). The measurements were carried out at room temperature using an excitation wavelength of 325 nm. The PL spectra is shown below.
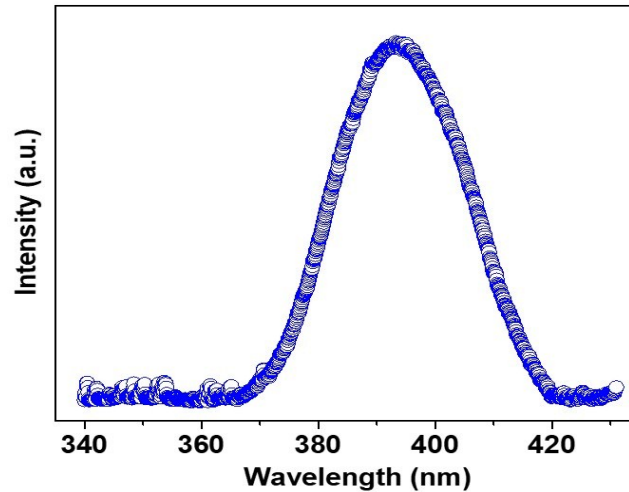

Figure S2: Photoluminescence spectra of the S3 film.

The PL peak at 3.13 eV for zirconia corresponds to F and F^+ color centers i.e. oxygen vacancies with charge states of -2 and -1 respectively (Ref. 1). The appearance of an intense peak at ~ 394 nm (~ 3.15 eV) in the PL spectra therefore indicates the presence of oxygen vacancies in the S3 film with a charge state of -2 and/or -1. This justifies the presence of the charged vacancies in the S3 film as predicted from our simulation results.

Gibbs free energy of formation of tetragonal and monoclinic zirconia nanoclusters

We have first modelled nanoclusters of monoclinic and tetragonal zirconia consisting of 102 atoms ($Zr_{34}O_{68}$) and 127 ($Zr_{43}O_{84}$) atoms respectively. After that, we have created two oxygen vacancies in both the modelled clusters. To investigate the stability, we have then determined (using eqn. (1), see manuscript) the free energy of formation (under ambient conditions (T=300K, p_o = 1atm)). The results are plotted in the figure below where the formation energy of the cubic nano-cluster is also shown for comparison. In contrary to the cubic phase, clusters of monoclinic and tetragonal

phase show positive formation energy. We can hence state that at the environmental condition of our interest (T=300K, p_o = 1atm), (a) oxygen vacancies are favored to form in the cubic clusters, and (b) not favored to form in tetragonal and monoclinic clusters.
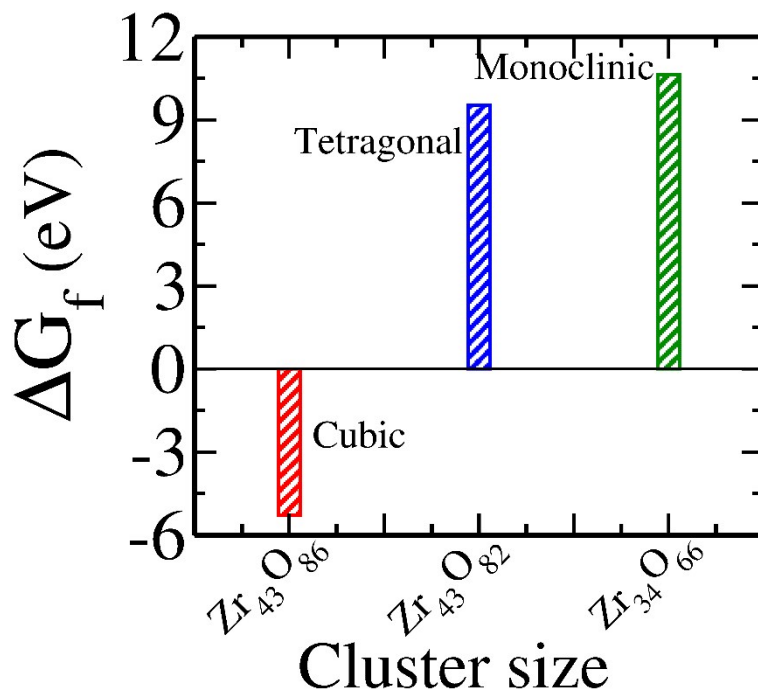
Figure S3: The formation energy for O-deficient nanoclusters of monoclinic (green bar), tetragonal (blue bar) and cubic (red bar) phases. The reference (zero energy) level, in each case, corresponds to the formation energy of the respective pristine (i.e. without vacancies) nanocluster.

References

1) Gurudayal, A. K. Srivastava and J. Kumar, *Materials Letters*, 2012, **83**, 172-174.