Supporting Information for

Molecular Dynamics Simulations, Thermodynamic Analysis and Experimental Study of Phase Stability of Zinc Sulfide Nanoparticles

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1. Dynamic relaxation and reconstruction of sphalerite (100) surface by MD at room temperature

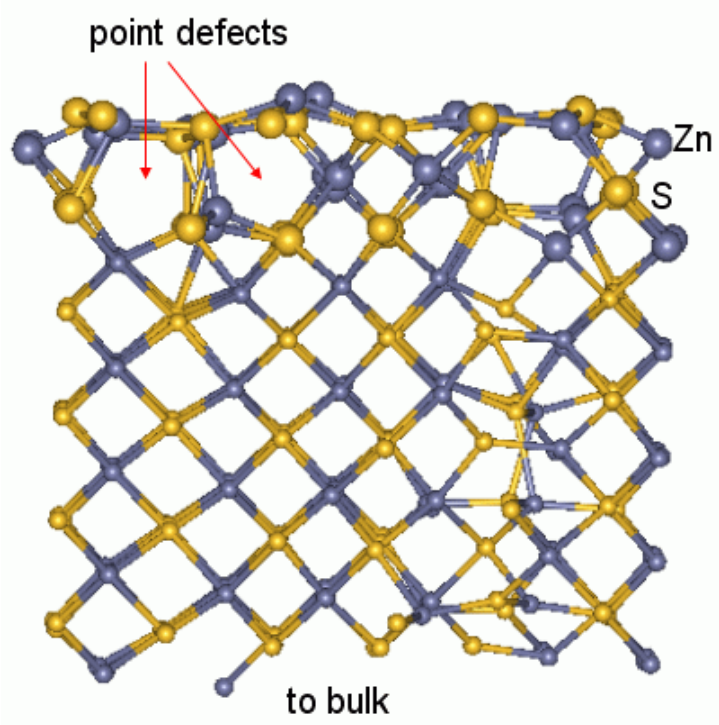

Figure S.1 Side view of sphalerite S-rich (100) surface dynamically relaxed by MD at room temperature. The surface is relaxed both by relaxation (shortening in layer distance) and reconstruction (repositioning) of atoms. Point defects near the surface are created as a result of the reconstruction. (Bigger balls: atoms on or near the surface).

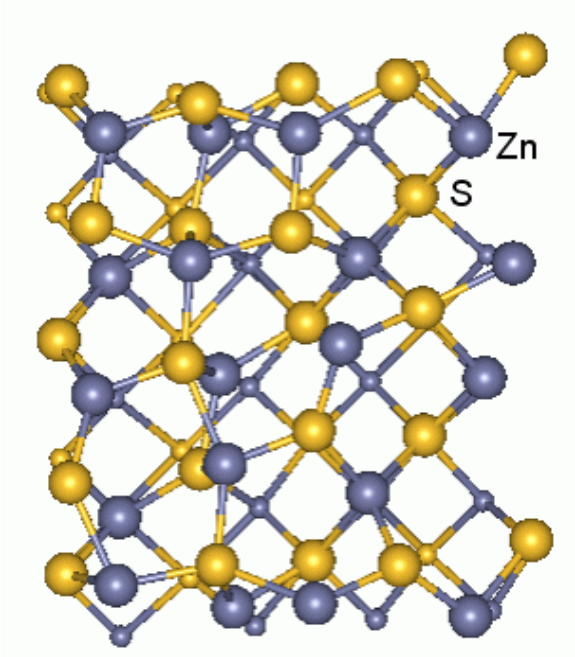

Figure S.2 Top view of sphalerite S-rich (100) surface dynamically relaxed by MD at room temperature. Due to the reconstruction, surface atoms do not have exactly the same lattice arrangements as in the bulk. (Bigger balls: atoms on or near the surface).

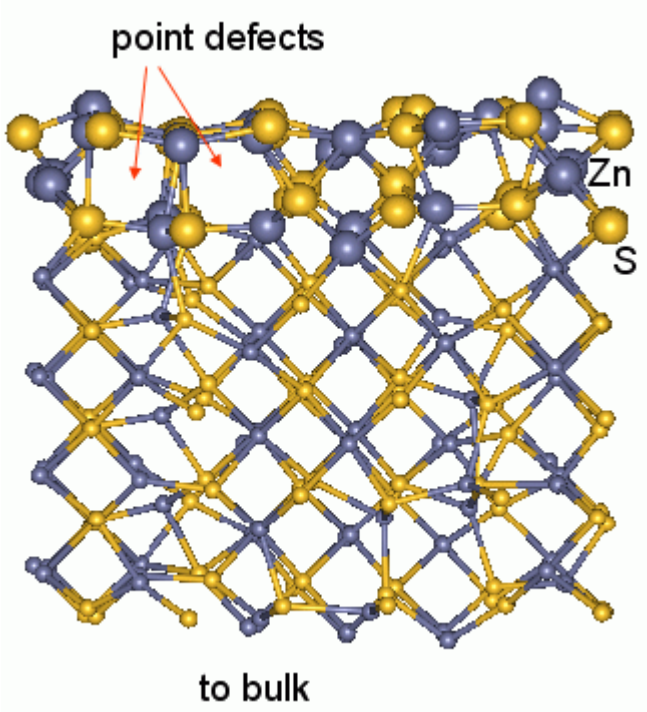

Figure S.3 Side view of sphalerite Zn-rich (100) surface dynamically relaxed by MD at room temperature. The surface is relaxed both by relaxation (shortening in layer distance) and reconstruction (repositioning) of atoms. Point defects near the surface are created as a result of the reconstruction. (Bigger balls: atoms on or near the surface).

2. Calculated Wulff shape of a sphalerite crystal

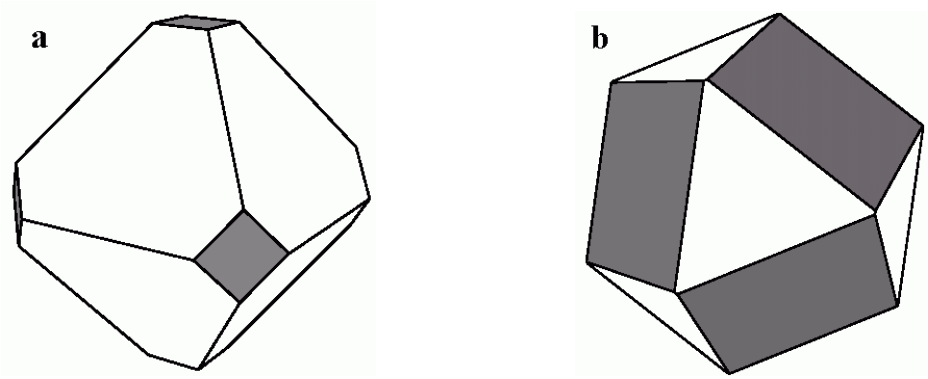

Figure S.4. Calculated morphology of a sphalerite crystal bounded by 6 {100} faces (shaded gray), 4 {111} faces and 4 {1 $\bar{1}$1} faces using surface energies from present work (a) or from ref.1 (b). The Wulffman program [2] was used in the calculation.

3. Comparison between MD results of the adsorption of water molecules on a 2 nm spherical ZnS (sphalerite) particle, with water molecules described by the SPCE [3] CF [4] and the shell [5] models.

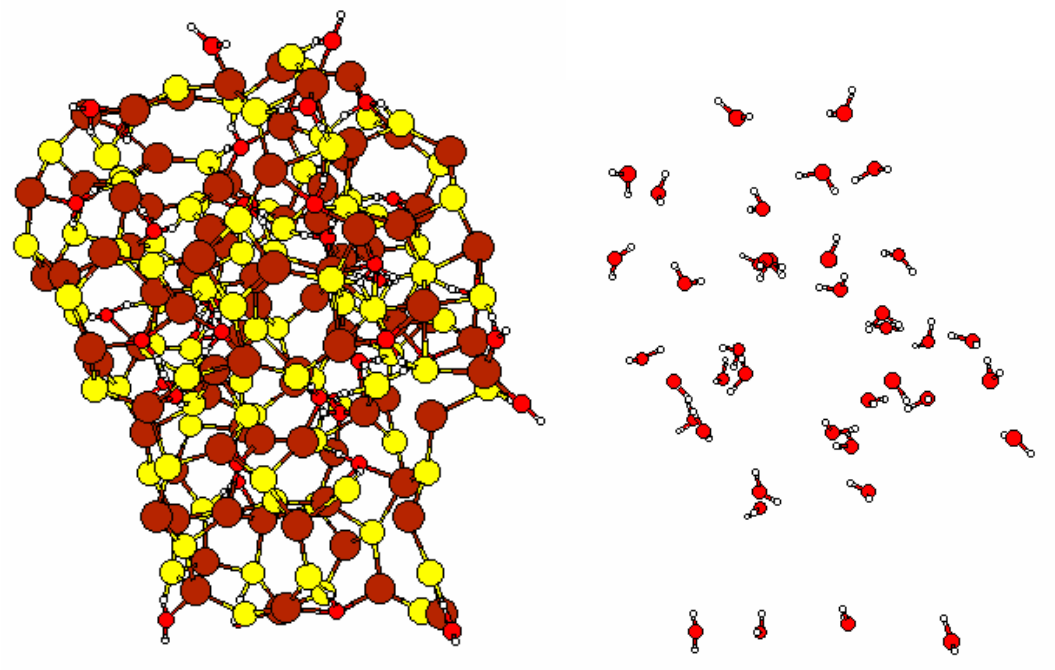

Figure S.5 Equilibrated shape of the ZnS nanoparticle after adsorption of 40 SPCE water molecules (left). Adsorbed water molecules are shown on the right alone. The nanoparticle is highly distorted. Water molecules are not dissociated. (Zn atoms are shown in brown, S in yellow, O in red and H in while circles).

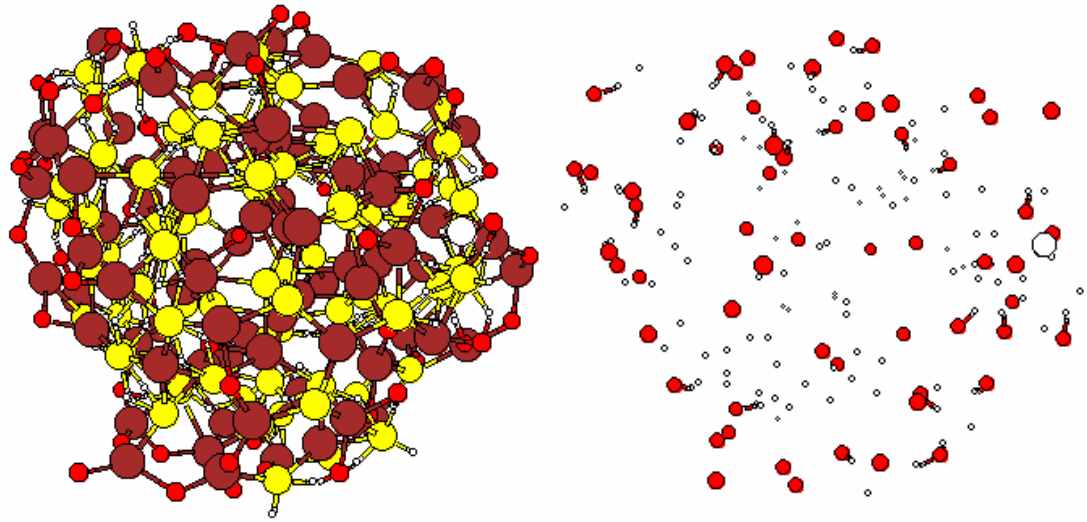

Figure S.6 Equilibrated shape of the ZnS nanoparticle after adsorption of 61 CF water molecules (left). Adsorbed water molecules are shown on the right alone. The nanoparticle is slightly distorted. Water molecules are strongly dissociated. (Zn atoms are shown in brown, S in yellow, O in red and H in while circles).

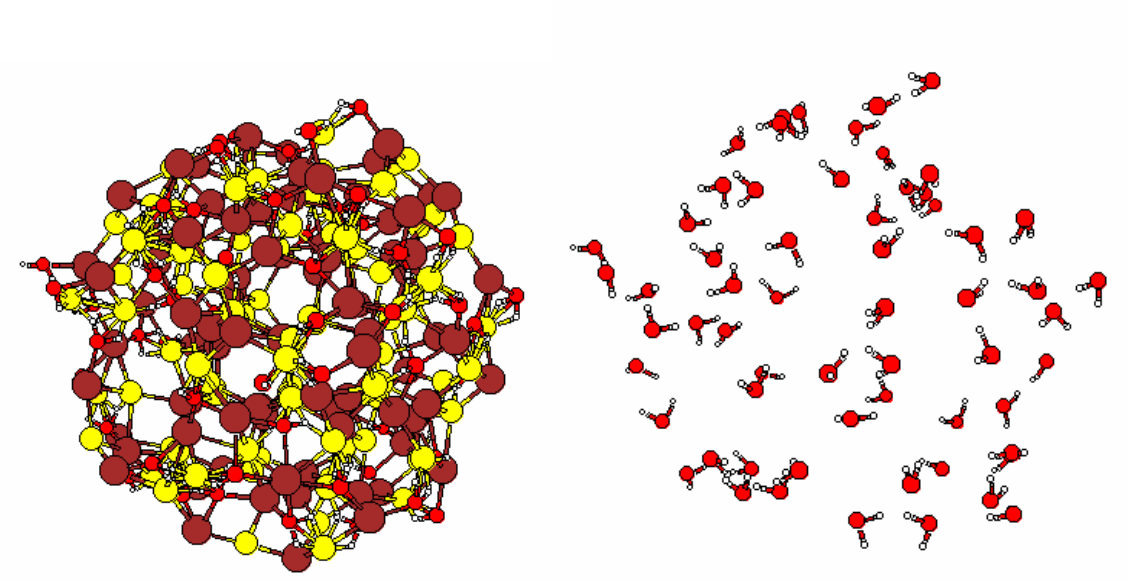

Figure S.7 Equilibrated shape of the ZnS nanoparticle after adsorption of 61 shell model water molecules (left). Adsorbed water molecules are shown on the right alone. The nanoparticle essentially keeps the spherical shape. Water molecules are not dissociated. (Zn atoms are shown in brown, S in yellow, O in red and H in while circles).

References

(1) Wright, K., Watson, G. W., Parker, S. C., and Vaughan, D. J., *Am. Mineral.*, **83**, 141, 1998.
(2) Roosen, A., McCormack, R. and Carter, W. C., Wulffman –An Interactive Crystal Shape Constructor, Center for Theoretical and Computational Materials Science, NIST, 1997. Available from the Internet at http://www.ctcms.nist.gov/wulffman.
(3) Berendsen, H. J. C., Grigera, J. R. and Straatsma, T. P., *J. Phys. Chem.*, **91**, 6269, 1987.
(4) Stillinger, F. H. and Rahman, A., *Chem. Phys.*, **68**, 666, 1978.
(5) de Leeuw, N. H. and Parker, S. C., *Phys. Rev. B*, **58**, 13901, 1998.