

# Water-driven Structural Transformation in Nanoparticles at Room Temperature

H. Zhang, B. Gilbert, F. Huang, J.F. Banfield

Department of Earth and Planetary Sciences, University of California, Berkeley, CA, U.S.A.

## Introduction

Nanoscale materials and devices are a research subject of wide interest. Of particular interest are semiconductor nanoparticles, which are celebrated examples of quantum confinement used for color-tunable fluorescent dyes. In addition to having electronic effects, the small particle size can also affect the stability of structures because of the large surface area in nanoscale systems. It has been frequently observed that the crystal structures of the nanoparticles of some materials are not the same as the structures observed in macroscopic samples. In particular, molecular dynamics (MD) simulations predict that surface ligand strength could be a very significant factor in stabilizing nanoparticles in structures that are in a metastable phase (at room temperature and pressure) in bulk materials [1]. The work described here indicates that changes in the surface ligand environment may drive phase transitions in nanoparticles.

## Methods and Materials

ZnS nanoparticles that were 3 nm in size and synthesized in anhydrous methanol without a surface-capping ligand were used to test the idea that nanoparticles can undergo surface-driven structural transitions at room temperature. Wide angle x-ray scattering (WAXS) was performed at BESSRC beamline station 11-ID-C at the APS to analyze the structures of ZnS nanoparticles after synthesis in methanol and following the addition of water. MD simulations predict that water would interact strongly with the surface of ZnS nanoparticles. The high-energy, high-flux beamline enabled suspensions of ZnS nanoparticles to be analyzed *in situ*, so a carefully controlled surface environment was maintained. The acquisition of diffraction data to high  $Q$ -values ( $Q$  is the diffraction vector) allowed the nanoparticle structure to be analyzed via the real-space atomic pair distribution function (PDF).

## Results

Figure 1 shows that a major structural change can be observed when a small amount of water is added to a suspension of ZnS nanoparticles in methanol. The experimental WAXS and PDF data show that the

nanoparticles possess a highly distorted structure in methanol. The structure becomes more crystalline and approaches the bulk zinc blende structure after the addition of water. Transmission electron microscopy and uv-visible absorption spectroscopy indicated that there was no change in particle size after the addition of water. The x-ray scattering data were in good agreement with the MD simulations.

## Discussion

The data in Fig. 1 are believed to represent the first observation of a surface-driven, room-temperature structural transition in nanoparticles. The data indicate that the nanoparticle structure is not kinetically trapped but is responsive to environmental changes. If alternative ligands or solvents that stabilize alternative structures can be found, there may be post-synthesis routes to particular or uncommon structures. Given the strong influence of water, the structure and properties of environmental, technological, or extra-planetary nanoparticles may depend on the extent of hydration. In addition, any nanoscale material or component may be susceptible to unpredictable structural change if exposed to water or other adsorbates.

## Acknowledgments

Thanks to Y. Ren and M. Beno of the BESSRC collaborative access team. Financial support for this work came from the U.S. Department of Energy (DOE), a Lawrence Berkeley National Laboratory LDRD (laboratory-directed research and development) project, and the National Science Foundation. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. Reference 2 is the source for this article.

## References

- [1] H. Zhang, F. Huang, B. Gilbert, and J.F. Banfield, "Molecular dynamics simulations, thermodynamic analysis and experimental study of phase stability of zinc sulfide nanoparticles," *J. Phys. Chem. B* (in press, 2003).
- [2] H. Zhang, B. Gilbert, F. Huang, and J.F. Banfield, "Water-driven transformation of nanoparticle structure at room temperature," *Nature* **424**, 1025-1029 (2003).

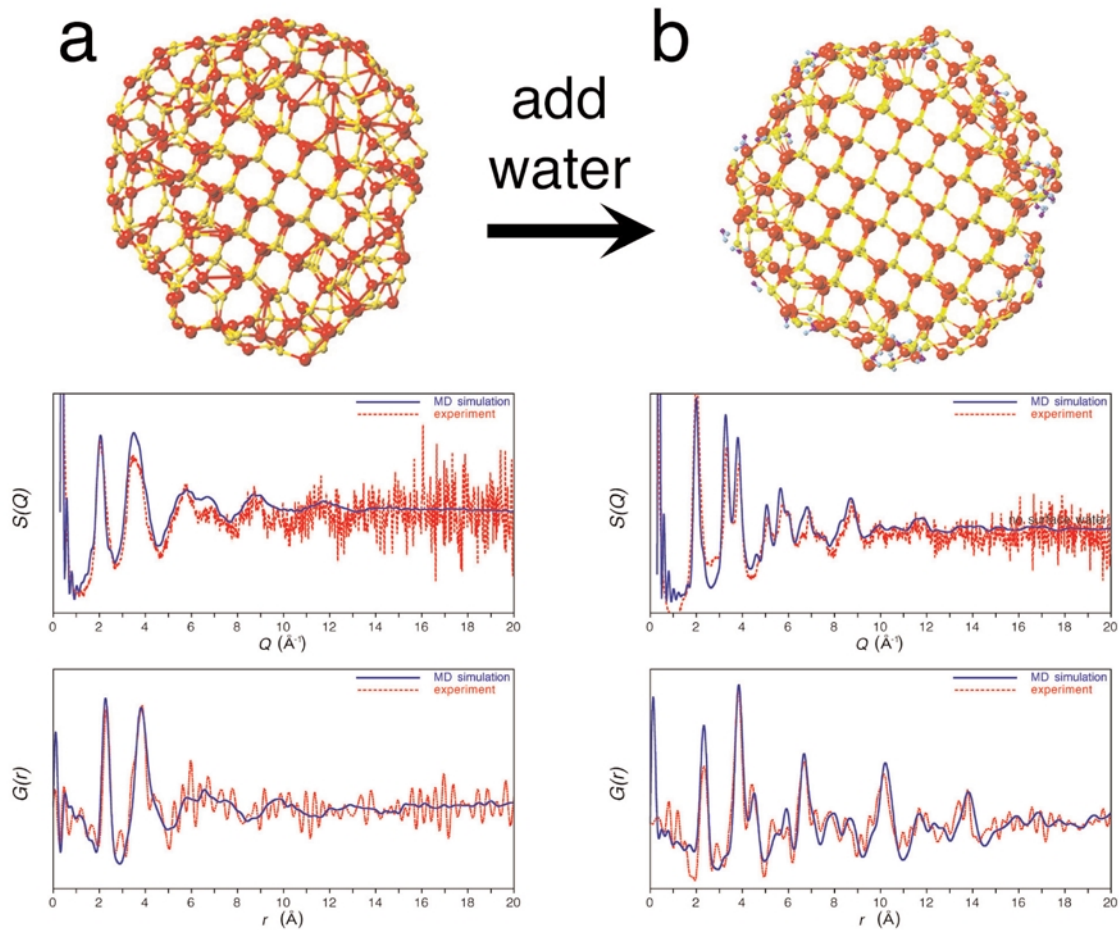


FIG. 1. Top: MD simulations predict that the addition of water to bare surfaces of ZnS nanoparticles would greatly increase internal crystallinity. The central cross sections showing the 110 plane that are pictured above reveal the interior structure better. S atoms are yellow, Zn are red, O are blue, and H are light blue. Cross section a shows that in the absence of water ligands, the nanoparticle structure is highly distorted. Cross section b shows that water binding produces a more crystalline interior structure. Bottom: WAXS measurements provided experimental confirmation that the addition of water can drive a room-temperature structural transition in 3-nm ZnS nanoparticles in methanol. There is excellent agreement between the experiment (red curves) and MD simulations (blue curves) for the diffraction structure factors  $S(Q)$  and the real-space PDFs  $G(r)$ .