Identifying Structure of GeOx Nanoparticles with XAFS

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GeO_x nanoparticles (NPs) are of growing interest in lithium storage and optoelectronics. We prepare GeO_x NPs by chemical reduction, expose them to air or retain them under N_2, then anneal under H_2 at various temperatures. We characterize these GeO_x NPs using hard and soft X-ray spectroscopy. The oxygen K-edge XANES exhibit a rich variety features, many not found in pristine GeO_2, that vary depending on exposure and annealing; we use density functional theory to identify the types of defects responsible for these features. The germanium K-edge EXAFS reveals Ge-O and Ge-Ge bonding, indicating the relative compositions of GeO_2, sub-stiochiometric GeO_x, and metallic Ge in these NPs. We find that fresh and air-exposed GeO_x NPs evolve rather differently under annealing: the fresh GeO_x NPs start as a very amorphous heterogeneous mixture of GeO_x and Ge, during annealing both the valence band and conduction band edges evolve. In contrast, air-exposed GeO_x NPs initially contain quartz-phase GeO_2, during annealing only the conduction band edge evolves due to increased oxygen vacancies forming unoccupied defect states. In this case the valence band does not change until annealing at high temperature, at which almost all the GeO_2 is removed. Our research suggests the preparation and annealing strategy that should be used to tailor GeO_x NPs for depending on their intended use in lithium storage or optoelectronic applications, and demonstrates the utility of X-ray spectroscopy and density functional theory in conclusively identifying the type of structural defect present in these oxides.

1. J. Zhao, L. Yang, J.A. Mcleod, and L. Liu, *Sci. Rep*. **5**, 17779 (2015).
2. J.A. McLeod, J. Zhao, L. Yang, Y. Liu, and L. Liu, *Phys. Chem. Chem. Phys*. **19**, 3182 (2017).