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Unraveling the mechanism of iron sulfide nanostructures formation: insights from *in situ* X-ray diffraction and spectroscopy studies

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Iron sulfides (Fe_xS_y) have emerged as promising materials for several applications. In particular, Fe_3S_4 greigite has attracted significant attention due to its magnetic properties and potential use in Li-ion and Na-ion batteries.[1] However, controlling the phase during the synthesis of the Fe_xS_y nanostructures remains challenging due to the system's complexity, with seven major crystal phases exhibiting different oxidation states and stoichiometries.[2] Understanding the chemical processes occurring during synthesis is crucial for obtaining a high-purity phase, which directly impacts the performance of the Fe_xS_y nanomaterials in the intended applications.

Here, we illustrate how combining *in situ* X-ray diffraction and spectroscopy studies offers insights into the formation mechanism of Fe_3S_4 nanosheets in solution under solvothermal conditions. Initially, *in situ* X-ray diffraction (XRD) uncovers the lack of long-range ordering in the initial stages of the reaction, followed by the initial crystallization of tetrahedral FeS phase (mackinawite) with preferred orientation along (001) plane, forming a layered structure. This phase gradually transforms into crystalline spinel Fe_3S_4 (greigite).

Using *in situ* high-energy resolution fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS) measurements, we identify four key components in the reaction: the iron(III) acetylacetonate precursor as the starting point, two distinct intermediates, and the final product, Fe_3S_4. The combination of HERFD-XAS and density functional theory (DFT) calculations suggests an initial reduction of the organo-metallic iron precursor with the simultaneous coordination of two benzyl alcohol solvent molecules, forming the first reaction intermediate. This oxygen-coordinated molecular intermediate then transforms into a tetrahedrally sulfur-coordinated compound that we identify as FeS through FEFF calculations, corresponding to the second intermediate in the reaction. Additionally, we employ an innovative approach using *in situ* valence-to-core X-ray emission spectroscopy (vtc-XES) at elevated temperatures in solution,[3] pinpointing the transition from the Fe-O to Fe-S coordination as the reaction progresses.

With the versatile combination of X-ray techniques, we obtain mechanistic insights into all steps of the complex formation of Fe_3S_4 nanosheets under solvothermal conditions.

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