

Colloidal synthesis and (meta)stability of 1T' TMD monolayers

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Group VI transition metal dichalcogenide (TMD) monolayers have attracted considerable attention due to their exceptional optoelectronic properties, which arise from their stable hexagonal crystal structure (1H phase), characterized by trigonal prismatic coordination of the transition metal atoms. Beyond this conventional phase, alternative crystal structures such as the metastable 1T' phase, where metal atoms adopt distorted octahedral coordination, are emerging as a promising research direction. These unconventional phases exhibit intriguing properties including metallic or semi-metallic behavior, superconductivity, and enhanced catalytic activity. However, current synthetic approaches remain limited, particularly with respect to achieving high-quality materials and scalable production.

To address this challenge, we have developed colloidal synthetic strategies to directly produce metastable 1T' TMD nano-monolayers (NMLs). This approach enables the synthesis of tungsten disulfide (WS₂) NMLs [1], as well as alloys (WSe_{2-x}S_{2-2x}) [2] and radial heterostructures, while providing control over the lateral size and dispersion of the NMLs from a few nanometers up to hundreds of nanometers.

Here we investigate the temperature-induced 1T'/1H phase transition in colloiddally synthesized WS₂ NMLs functionalized with organic ligands. [3] The strongly reducing conditions of the synthesis stabilize the 1T' phase through electron doping. By combining in situ structural and spectroscopic analyses, we monitor the phase evolution during annealing. We find that the 1T' phase remains stable up to 300 °C, accompanied by a slight lattice contraction. Between 300 °C and 350 °C, a mixed 1T'/1H regime emerges in which the relative 1H fraction can be finely tuned through the annealing time. Above 350 °C, a rapid and complete transformation to the semiconducting 1H phase occurs. We show that the decomposition of the reducing ligands acts as the primary trigger for the structural transition, revealing a strong interplay between charge doping, surface chemistry, and lattice structure.

The strategy demonstrated here for WS₂ can be readily extended to other metastable colloidal TMD systems and provides new insight into the role of composition and surface chemistry in stabilizing the 1T' phase. More broadly, this work highlights how chemically driven and thermally activated processes govern phase behavior in colloidal TMD nanostructures, offering new routes for phase engineering through ligand and thermal control.

References

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