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Atomic Resolution STEM Imaging of Novel Van der Waals Materials Synthesized by Soft Chemical Methods

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Van der Waals materials are an indispensable part of functional device technology due to their versatile physical properties and ease of exfoliating to the low-dimensional limit. Among all the compounds investigated so far, the search for magnetic Van der Waals materials has intensified in recent years, fueled by the realization of magnetism in two dimensions (2D) [1-3]. Cation deintercalation with soft-chemical methods provides a route to synthesize new layered compounds with emergent physical and chemical properties that are inaccessible by conventional high-temperature solid-state synthesis methods. One example is $CrSe_2$, a van der Waals (vdW) material that is promising as an air-stable 2D magnet. Cation deintercalation has rarely been studied mechanistically, and optimized reaction pathways to yield high-quality materials are often poorly understood. Here, we performed a detailed study of the oxidative deintercalation process of $NaCrS_2$ [1] and $KCrSe_2$ [3] and the final products by using high-resolution scanning transmission electron microscopy (STEM) and electron dispersive spectroscopy (EDS) (no beam damage issue [4]).

Figure 1 showed STEM imaging of Van der Waals-layered structure of CrS_2. We revealed a complex structure consisting of alternating layers of amorphous and crystalline lamellae in a new CrS_2-based crystalline/amorphous layered material synthesized by soft chemical methods. This material can be exfoliated, thus providing a facile synthesis method for chromium-sulfide-based ultrathin layers. On the other hand, we studied the kinetics of the oxidative deintercalation process of $KCrSe_2$, showing that it is a zeroth-order reaction with an activation energy of 0.27(6) eV, where the solid-state diffusion of K+ cations in the potassium deintercalation process is the rate-limiting step. We investigated the relationship between Cr–Cr distances and the change in magnetic order by tracking how the properties change as a function of varying potassium content due to deintercalation [5].

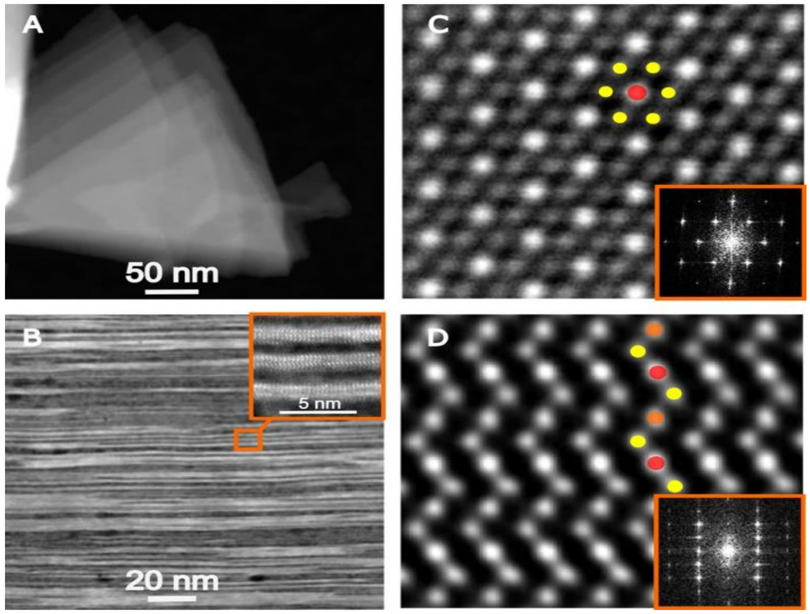

Figure 1. STEM imaging of Van der Waals-layered structure of CrS_2. (A) the loosely layered structure viewing on top of the planes, zone axis [001]. (B) the cross-sectional structure viewing from zone axis [110]. Crystalline planes are clearly shown as bright stripes in the image. The inset is a magnified image showing the layered structure with periodic arrangement of amorphous and crystalline phases marked in panel B. (C, D) the in-plane and out-of-plane structures, respectively. The insets are the corresponding Fourier filtered diffraction patterns. The S, Cr, and the migrated Cr atoms are indicated by the yellow, red, and orange spheres, respectively.

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