

Lithium Electrochemistry of WS₂ Nanoflakes Studied by In-situ TEM

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Layered tungsten disulfide (WS₂) shows a unique combination of valuable structural, electronic, optical, mechanical, chemical, and thermal properties that have been studied for decades [1]. The large interlayer separation in WS₂ (~0.65 nm) provides perfect locations to accommodate guest species such as alkali metal ions (Li⁺, Na⁺, and K⁺) through a process known as intercalation. Intercalation in layer-structured materials such as MoS₂ have been extensively studied for applications in energy storage [2-4]. Unlike MoS₂, WS₂ has large lattice parameters and smaller bandgap, which indicates that its better electrochemistry performance but current research lacks. Recent developments of *in-situ* transmission electron microscopy (TEM), as one unique tool to conduct real time structural measurements under the dynamic electrochemical reaction processes [5]. Such *in-operando* measurements make it possible to analyze and tackle the intricacies of the lithiation mechanism in electrode materials during charge/discharge cycles. Herein, we applied both the *in-situ* electron diffraction with a remarkably low electron beam dosage and atomic resolution TEM (HRTEM) images to view along the same crystallographic direction and study the dynamic structural evolutions of lithium intercalated WS₂ nanoflakes during lithiation. The electron diffraction patterns is then carefully compared to the HRTEM results to identify the beam effect on WS₂ nanoflakes. It is to study the dynamic and structural evolutions and unravel the mechanism of WS₂ lithiation.

Figure 1 shows the pristine state (a-c) and lithiated (d-f) WS₂ nanoflakes. Electron diffraction pattern of the pristine WS₂ indicates a nature of perfect single crystal. After lithiation, the WS₂ nanoflake is converted to Li₂S and W nanoparticles. In addition, there is also an in-plane expansion around 16.6%. As shown in Figure 2 (a-f), the time-lapse electron diffraction patterns (EDPs) of WS₂ nanoflake acquired along the [001] zone-axis after the reaction time of 0, 120, 210, 220, 240, 300 seconds, respectively. The [001] zone axis EDP of the pristine 2H-WS₂ (Figure 2(a)) shows one set of 6-fold symmetry diffraction spots. After 120s of lithiation, the (100) lattice *d*-spacing is gradually increased corresponding to the gradually increase of intercalated lithium. At 210s, surprisingly, the extra spots start to appear as indicated by green arrow. At 220s, the diffraction spots corresponding to a commensurate superstructure become much clearer (Figure 2(e)). At 240s, the newly appeared diffraction spot as indicated by yellow arrow indicates the formation of Li₂S. Finally, the fully lithiated WS₂ nanoflake is converted to Li₂S and W nanoparticles without any lithium-intercalated superstructure (Figure 2(f)). This structural evolution can be described by a two-step reaction: intercalation reaction followed by conversion reaction. A phase transformation from 2H-1T can be identified at the intercalating stage. Moreover, the EDPs results are coincide with HRTEM results very well, which means WS₂ nanoflake is relatively stable under the electron beam irradiation.

The presentation will also cover ongoing investigations and data analysis; all of which may provide further insights into the understanding of the lithiation kinetics and mechanisms in typical layered transition-metal dichalcogenide structures. We believe these will be helpful in designing next generation advanced lithium ion batteries [6].

References:

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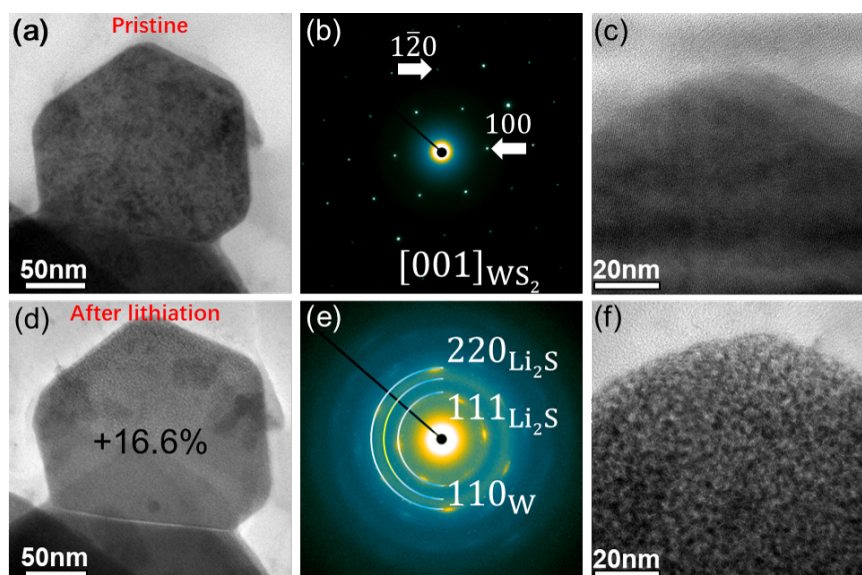


Figure 1. Lithiation of WS₂. (a-c) Pristine state of WS₂ nanoflake. (d-f) Lithiated WS₂.

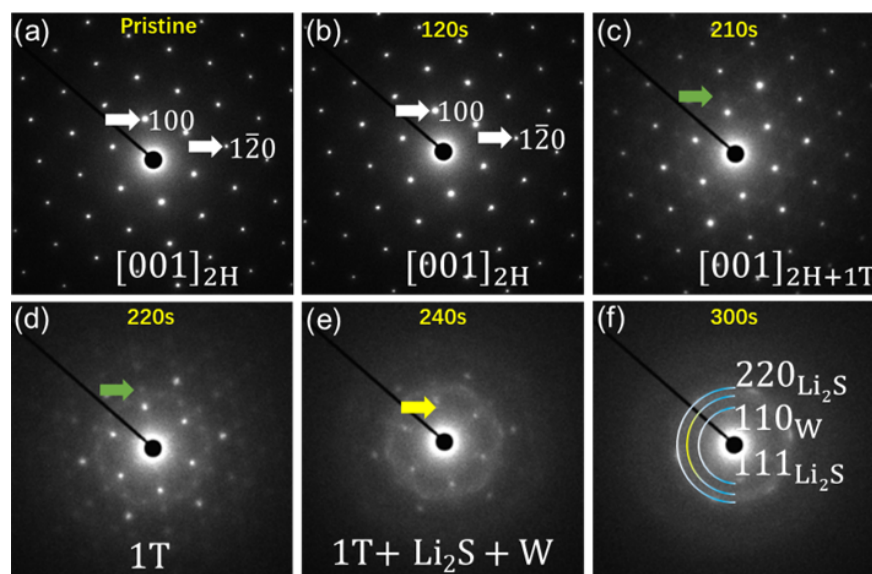


Figure 2. *In-situ* electron diffraction of WS₂ lithiation. (a-f) *In-situ* electron diffraction patterns (EDPs) along the [001] zone-axis during the lithiation process.