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In-situ TEM Studies of Structural Modification in WS_2 during Intercalation of Li and Na

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Understanding the atomic scale processes during intercalation of alkali metal ions with transition metal dichalcogenides (TMDs) materials is important owing to their potential application as possible anode materials for solid-state batteries (Yu, et al., 2019). This has laid the new strategies in terms of novel experimental design catalyzed by availability of novel commercial TEM holders for in-situ investigations (Carter & Williams, 2016). Tungsten disulfide (WS2), with a large van der Wall gap (~ 0.65 nm) affords to accommodate alkali metal ions (Li+, Na+, and K+) through intercalation. Intercalation in MoS2 has been extensively studied for its applications in storage of energy (Sun, et al., 2019). The WS2, in spite of having larger lattice parameters has received lesser attention compared to that of MoS2. It has been reported earlier that despite larger interlayer separation in WS2 than that of MoS2, greater quantity of Li intercalates in MoS2. The amount of Li was found to increase with temperature in WS2 (Yang & Frindt, 1996). The rationale behind this preferential nature of Li intercalation in the two isostructural layered materials is not understood well. The formation of L2S and W nanoparticles has been reported during intercalation of WS2 nanoflakes with Li as observed using in-situ TEM (Xu, et al., 2018). Herein, in-situ TEM has been employed to study the dynamics of structural evolutions of mechanically exfoliated WS2 during the solid-state reactions of Li and Na. The post-reacted specimens are characterized in detail for their structures and chemistry through SADP, HRTEM, HR-EELS and compared with pre-reacted specimens. The experimental observations are compared with computer modeling.

Solid state reactions of Li and Na with WS2 have been carried out inside a FEI Tecnai F30 in-situ employing Nanofactory TEM- STM holder (Ghosh, et al., 2020; Singh, et al., 2020). The structural characterization of pre- and post-intercalated specimens have been performed through selected area electron diffraction (SAD) and HRTEM. The chemistry of WS2 after Li and Na reactions have been studied using EELS and STEM-XEDS.

Figure 1 shows the BF-TEM images and electron diffraction patterns of mechanically exfoliated WS2 before and after reaction with Li. The WS2 shows layered contrast prior to intercalation and this can be due to creation of strain during mechanical exfoliation (cf. Fig. 1a). SADP recorded from pre-reacted WS2 shows spots (0 1 $\bar{1}$ 2) and (1 1 $\bar{2}$ 2), conforming to the single crystalline nature of the sample (Fig. 1b). These spots could be indexed to those of 2H-WS2 phase. Diffraction pattern obtained from post-intercalated WS2 shown in Figure 1(d), displays several extra reflections apart from the 2H-WS2, clearly suggests the formation of new phases. Two distinct phases have been observed, spots corresponding to LixWS2 and orthorhombic Li2S are marked. BF micrograph of the WS2 after Li-intercalation appears to have no contrast and this can be ascribed to strain relaxation during Li-intercalation (Fig. 1c). Moreover, a distinct microstructural change has been observed in the WS2 after Li intercalation; the initially extended grains present in pre-reacted specimen got fragmented during the intercalation process. This is supported by the appearance of streaking in the principal reflections of 2H-WS2 and has also been substantiated with high-resolution phase contrast images. The same region of the reacted specimen was examined for chemical and structural changes.

The presentation will also include ongoing experiments, data analysis and computer modeling. These may facilitate to gain further insights to unearth the mechanisms of intercalation in TMDs.

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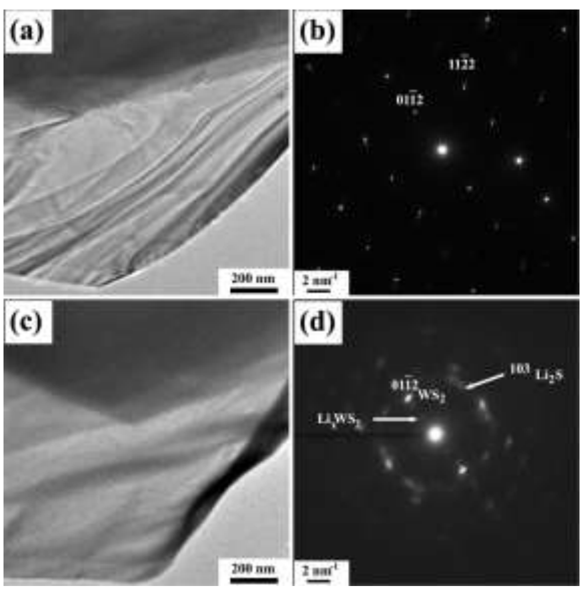

Figure 1. Bright-field TEM micrographs and corresponding selected area electron diffraction patterns of WS2 prior to (a, b) and after Li intercalation (c, d).

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