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Anisotropic Lithiation and Sodiation of ReS_2 Studied by *In-situ* TEM

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Crystalline structure and composition of the electrode materials determine the electrochemical performance of the lithium-ion and sodium-ions batteries. It has been observed that the performance of batteries is influenced by the crystallographic orientation of the electrode materials, especially the surface exposing to the electrolyte which has been facilitating the electrode/electrolyte interaction and the transportation of the lithium-ions. For instance, anatase TiO_2 crystals with the (001) facets has an enhanced lithiation performance compared to randomly oriented crystals, possibly due to a more favorable Li insertion and a facile Li diffusion along the [001] direction [1]. Among the layer-structured transition metal dichalcogenides, two-dimensional (2D) rhenium disulfide (ReS_2) has the largest anisotropic ratio between the two main axes and a very weak interlayer coupling, which serves as an ideal sample to observe the anisotropic electrochemical reactions with lithium and sodium ions. ReS_2 has extremely weak van der Waals interlayer coupling of ~18 meV per unit cell (for comparison, 460 meV for MoS2 per 2×2 conventional cell) [2]. All of the properties especially the weak interlayer coupling provide new opportunities for massive Li^+ and Na^+ to efficiently diffuse inside of ReS_2 structure, with great potential application in high-current-density rechargeable batteries.

Here, by *in-situ* transmission electron microscopy (TEM), such anisotropic lithiation and sodiation has been observed from liquid-phase exfoliated ReS_2 dispersions at high resolution to discover the reaction mechanism. As shown in Fig.1 (a-b), the area expansion of a ReS_2 crystal oriented closed to the [100] axis after sodiation (Fig.1b) is measured and compared to that before sodiation (Fig.1a). The crystal expanded greatly along the [001] axis which is the normal of the ReS_2 layers, *i.e.* from ~77 nm to ~161 nm with ~109% elongation in the crystallographic orientation perpendicular to the ReS_2 layers. In comparison, there is only ~19% elongation along the [010] axis. From an in-plane oriented ReS_2 crystal (Fig.1c), the elongation along the [100] axis is about ~10% (expanded from ~73 nm to ~80 nm). With ReS_2 layer (thus the (001) lattice plane) as the reference plane, the out-of-plane expansion is almost 10 times larger than that of in-plane expansion, which demonstrates clearly the anisotropic character of sodiation.

Complemented with density functional theory (DFT) calculations, the lithiation of ReS_2 has been found to begin with intercalation of Li-ions among the ReS_2 layers (up to 2 lithium), and be followed by a conversion reaction with products of Re fine nanoparticles embedded inside Li_2S nano-crystals. The reaction kinetics is highly anisotropic, fast along the ReS_2 layer (in plane) and slow along the interlayered (out-of-plane) direction. The sodiation of ReS_2 is found to proceed *via* a similar type of reaction with the lithiation counterpart while the intercalation step is relatively slower. The microstructure and morphology of the reaction products after lithiation/sodiation show clear anisotropy along the in-pane and out-of-plane directions. Therefore we suggest that the fast reaction direction (which is the crystallographic orientation with high electronic and ionic conductivity) should be aligned to the electric following direction of the battery charge/discharge circuit (so called 'through plane direction') to improve the electrochemical performance [3].

References:
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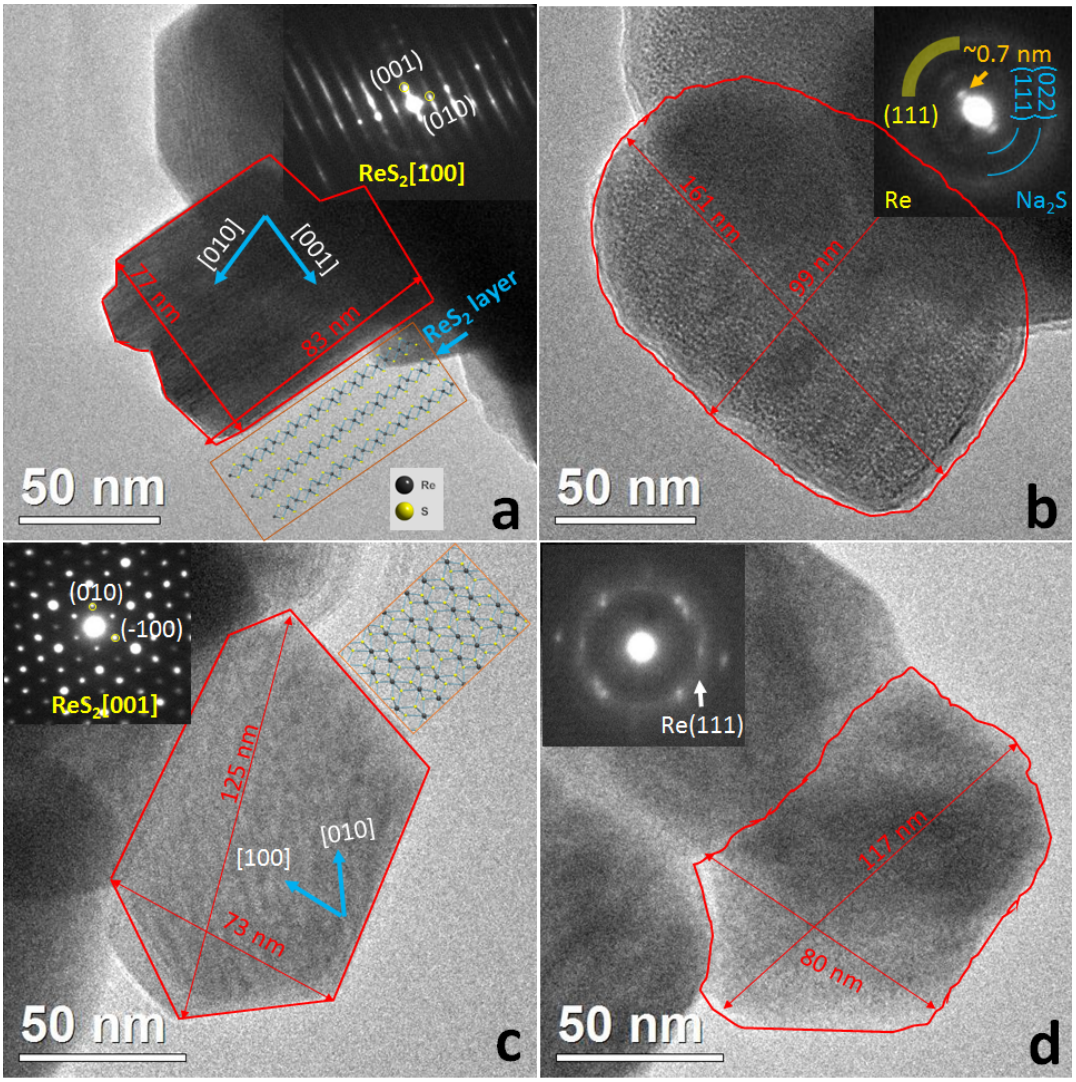

Figure 1. Directional sodiation of ReS_2. (a) The pristine ReS_2 crystal in the out-of-plane direction. The orientation is identified by the electron diffraction as insert. An illustration of ReS_2 structure and layers is also inserted. (b) The lithiated ReS_2 in the out-of-plane direction, showing changes in morphology, structure (by the inserted electron diffraction pattern). There is large expansion along the [001] direction. There is diffraction spots with d-spacing of ~0.7 nm, occurred by the modulated structure of Re-cluster and Na_2S lamellas. (c) The pristine ReS_2 crystal in the in-plane direction. The orientation is identified by the electron diffraction as insert. An illustration of ReS_2 structure and layers is inserted. (b) The lithiated ReS_2 in the in-plane direction, showing changes in morphology, structure (by the inserted electron diffraction pattern). There are several bright diffraction spots corresponding to Na_2S, meaning that the Na2S crystal is large and have preferred orientation along the in-plane direction.

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