Supporting Information

Atomic-Scale Clarification of Structural Transition of MoS_2 upon Sodium Intercalation

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Supporting results and discussion

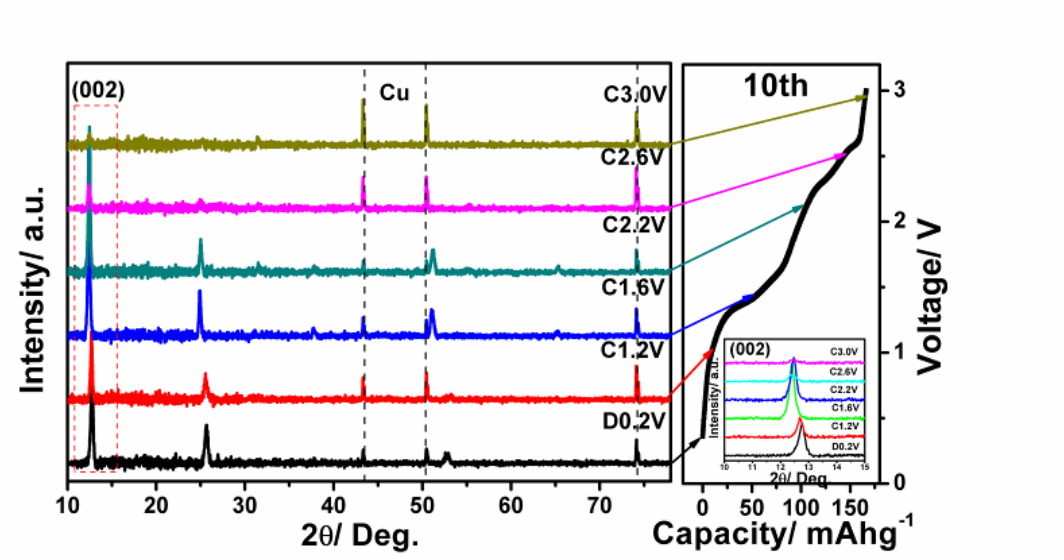

Figure S1. *Ex situ* XRD patterns of MoS_2 at various intercalation/deintercalation states after 10 cycles at a current density of 50 mA g^{-1} from 0.2 to 3.0 V. The inset is the magnification of the (002) diffraction peak. The positions of the peaks have been calibrated with that of Cu

current collector and the background of the protection film has been removed. The *ex situ* XRD results agree well with that of the *in situ* XRD (Figure 2b). Hexagonal Na_xMoS_2 is formed at 0.2 V and MoS_2 can be observed above 1.2 V, indicating that the structural change of MoS_2 in this voltage range is partially reversible.

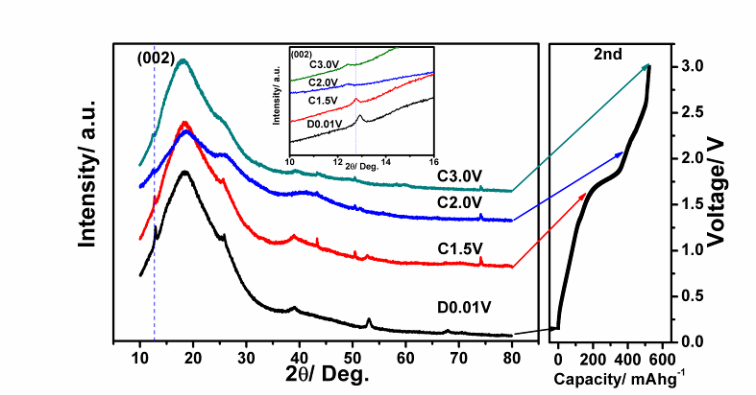

Figure S2. *Ex situ* XRD patterns of Na de-intercalated MoS_2 at a current density of 50 mA g^{-1} in the range of 0.01-3.00 V. The inset is the magnification of (002) diffraction peak (the broad peak at 18.51° comes from the protection film). It shows that once Na_xMoS_2 is decomposed to metallic Mo and Na_xS_2, no MoS_2 can be recovered up to 3.00 V.

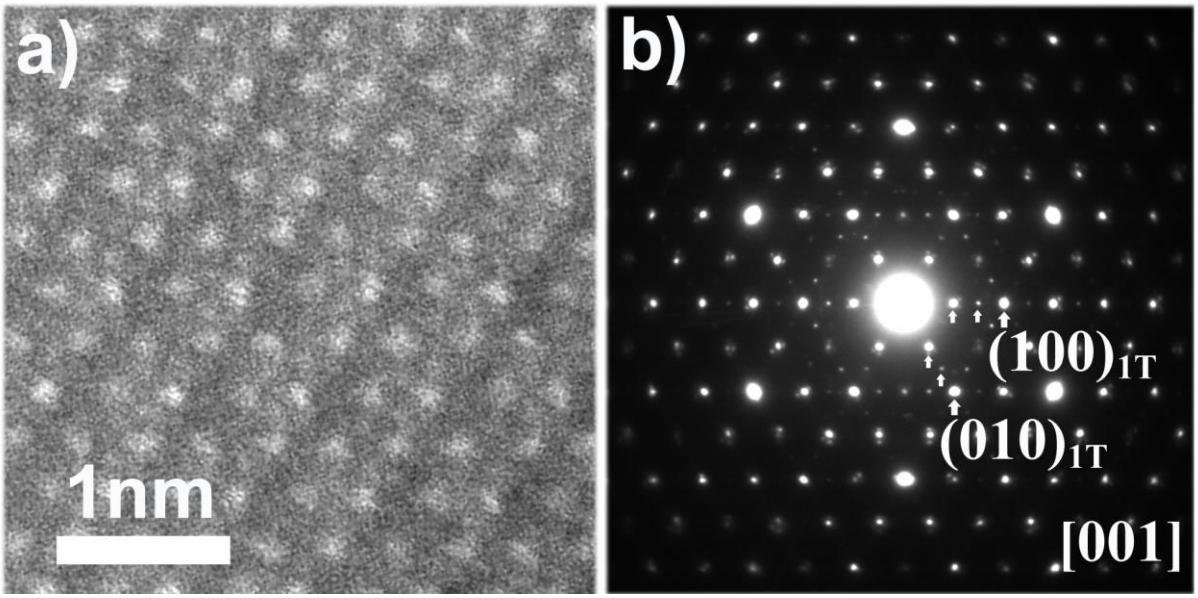

Figure S3. High-angle annular dark field (HAADF) image (a) and its selected area electron diffraction (SAED) pattern (b) of Cell-320 along [001] zone axis (commercial MoS_2 used). Figure S3b shows a 4×4 modulated structure, probably due to the formation of Mo zigzag-chain clusters (Ref. 30; J. Am. Chem. Soc. 2014, 136, 6693-7). The SAED pattern is indexed according to the 1T-MoS_2 structure.

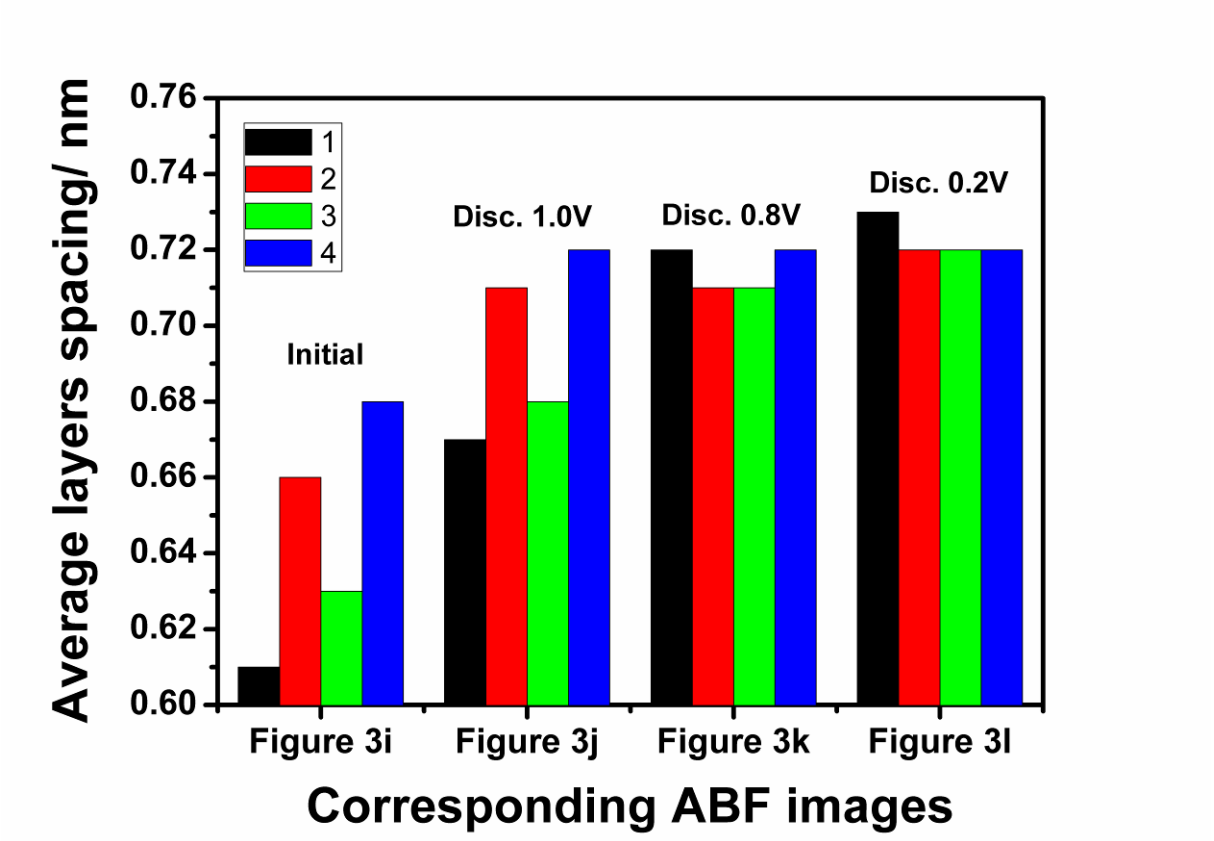

Figure S4. Average layers spacing of the as-prepared nano-MoS_2 (Figure 3i) with cutoff at 1.0 V (Figure 3j), 0.8 V (Figure 3k) and 0.2 V (Figure 3l). The numbers (1, 2 etc.) stand for the layers spacing from top to down in their corresponding annular bright-field (ABF) images of along the [100] zone axis. The average layers spacing of initial nano-MoS_2 is around 0.61~0.68 nm due to the distorted nanosheets. The Na-ion intercalations increase the spacing from 0.68 nm to 0.72 nm and the staggered spacing of nano-MoS_2 with cutoff at 1.0 V (Figure 3j) and the nearly spacing about 0.72 in Figure 3l indicate that the Na ions first intercalate in every other interlayer.

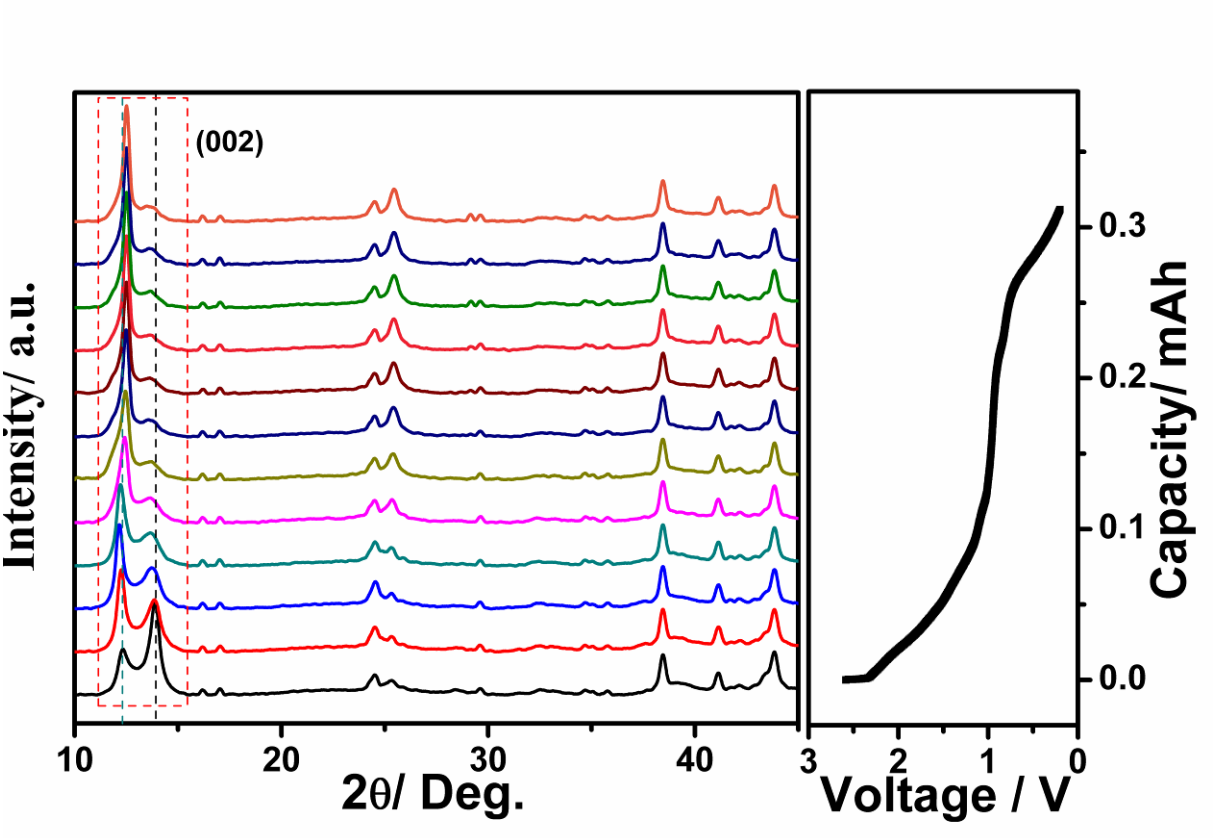

Figure S5. *In situ* XRD patterns of MoS_2 at various intercalations in the second cycle from 3.0 to 0.2 V. The subsequent Na-ion intercalation is similar to that in the first discharge process, and two apparent biphasic transitions occur during continual intercalation

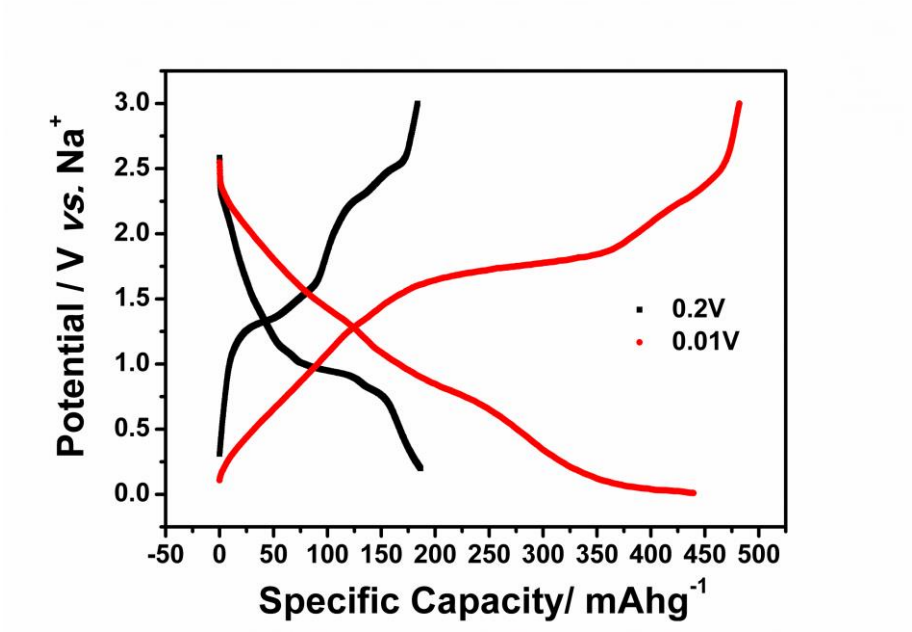

Figure S6. Potential profiles of MoS_2 with different cutoff voltage in the second cycle.