Local and electronic structure study of black phosphorus by XAFS

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Black phosphorus (BP) has attracted intense research attention as one promising anode material for lithium-ion batteries and sodium ion batteries due to its high theoretical capacity of 2595 mA h g^{-1}. However, several challenges impede the practical application of black phosphorus, including volume expansion, degradation in the air and unsatisfied electronic conductivity. In the case of the challenges in the degradation and electronic conductivity, the local and electronic structure play a crucial role, which can be studied by X-ray absorption fine structure (XAFS). Here, we report X-ray near edge spectra (XANES) and Extended X-ray absorption fine structure (EXAFS) studies of the local and electronic structure of oxidized BP and heteroatom-doped BP with a focus on the better understanding of the degradation and the band structure variation.

Black phosphorus and Se-doped black phosphorus (SeBP) were treated with different amount of water and oxygen controlled via the Atomic layer deposition (ALD). Then the treated BP samples and heteroatoms-doped BP samples were characterized by X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS).

In the degradation study of BP, BP treated with O_2 and H_2O demonstrated different oxidation states for phosphorus. Based on XPS and XANES result, the increased treatment time of O_2 and H_2O lead to gradually increased intensity of the oxidized BP spectra (~134 eV). In addition, BP treated with H_2O shows the oxidation state less than +5 and O_2 leads to stronger oxidation. As for the heteroatom-doped BP, XANES and EXAFS show that selenium has been successfully doped into black phosphorus and the crystal structure of black phosphorus remains intact . Due to the larger atomic radius of Se than P, the two peaks in R-space of SeBP shift to larger distance, illustrating a local expansion in the crystal.

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