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NEW PHOSPHORUS STRUCTURES: FROM TYPE-II RED PHOSPHORUS TO PHOSPHORENE EDGES

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Various allotropes and polymorphs of phosphorus have gained wide attention. In the first part of my talk, I will discuss our effort to identify the crystal structure of type-II red phosphorus (RP), which has not been solved for the last 70 years [1]. RP, an allotrope of phosphorus which is usually known to be amorphous, has several types of crystalline phases. The crystal structures of type-IV (fibrous RP) and type-V (Hittorf 's phosphorus) have been previously identified by single-crystal X-ray crystallography, however, those of type-II and type-III phases are yet to be identified. We identified the crystal structure of type-II RP using complementary characterization with power X-ray diffraction, 3D electron diffraction, and atomic-resolution scanning transmission electron microscopy (STEM) [2], as seen in Fig. 1. We confirmed that type-II RP has a large triclinic unit cell with approximately 500 phosphorus atoms. Moreover, STEM images clearly revealed the local tubular structure of phosphorus. In the second part of my talk, I will present on the modification of black phosphorus (BP) edges [3] using in situ heating under TEM imaging. We observed the formation of ultra-high stability zigzag phosphorene edges at elevated temperatures [4]. From the edge structure investigation, we found that the phosphorus atoms at edges are merged together to form closed zigzag phosphorene edges. We envision that these newly identified phosphorus structures facilitate various fundamental studies on phosphorus allotropes and polymorphs.

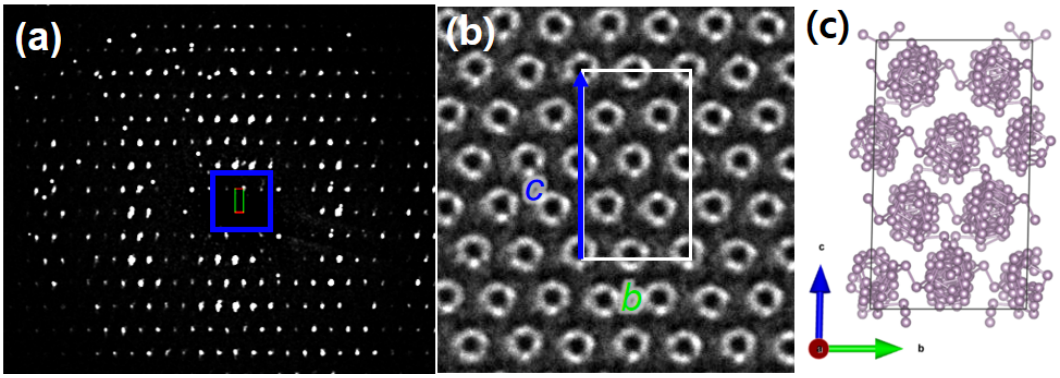

Figure 1. Structure characterization of type-II red phosphorus. (a) 3D electron diffraction, (b) Cross-sectional STEM image, (c) Atomic model of type-II red phosphorus

References

[1] W. L. Roth *et al.*, *J. Am. Chem. Soc.* **69**, 2881 (1947)
[2] J.-Y. Yoon *et al.*, unpublished.
[3] Y Lee *et al.*, *Nano Lett.* **20**, 559 (2020).
[4] S. Lee ***et al.***, unpublished.