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Safe and fast synthesis of black phosphorus and its purification

Following the mechanical exfoliation of graphene from graphite, investigation into other two dimensional materials sharply rises. To date, existence of hundreds of other 2D materials such as hexagonal boron nitride and transition metal dichalcogenides (TMDs) have been reported. Because of its flat structure and unique electronic and opto-electronic properties, the 2D materials has appeared as the materials for next generation technology. Among those 2D materials, thin layer of black phosphorus, also known as phosphorene, is one of the most promising materials for utilization in various types of devices because of it's tunable direct band gap depending on the number of layer, high carrier mobility, and strong in-plane anisotropy. Though the BP is the most stable among the three allotropes of the elemental phosphorus, it's the most costly because of the difficulty of its synthetic procedures. Indeed, one of the key challenges in materialization of the enormous opportunity in various application is the quick and cost effective bulk synthesis of pure black phosphorus.

Among the different synthetic procedures, high pressure-heating of white or red phosphorus, bismuth flux, and transport reaction method[1] are prominent. In transport reaction method (TRM), a definite ratios of red phosphorus, tin, and tin(Ⅳ) iodine is loaded in vacuum sealed silica ampule and heated to high temperature for a prolonged period of time followed by slow cooling of the ampule. The minimum time required to synthesize black P through TRM is reported to be about 23 hours. During the prolonged heating of red P in the sealed silica tube, the high pressure of gaseous P developed inside the tube sometimes lead to the explosion of the ampoule with evolution of huge fume and spreading of small pieces of glass. The explosion is found strong enough for physical injury if the proper protection gears is not used. The loading capacity of the silica tube and improper sealing of the ampoule is expected to be a key factor for the possible explosion. Here we report a safer and faster synthesis of black P without compromising quality and the reaction yield, and a simple physical and chemical method for cleaning the BP crystal obtained by CRT method. A typical black phosphorus crystal prepared in the present study and its Raman spectrum is shown in figure 1

References

[1] Ming Zhao, Haolei Qian, Xinyue Niu, Wei Wang, Liao Guan, Jian Sha, and Yewu Wang, *Cryst. Growth Des*. **2016**, 16, 1096−1103.

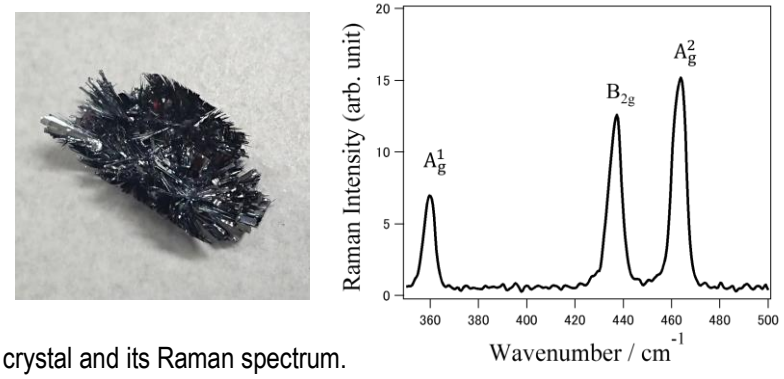

Figure 1. Photograph of black phosphorus crystal and its Raman spectrum.