# Efficient synthesis of pure bulk black phosphorus and high-quality exfoliation of phosphorene

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## Abstract

Black phosphorus (BP) is the most promising material among the two-dimensional (2D) materials thanks to its layered structure and excellent semiconducting properties. Currently, bulk BP flakes are synthesized under high pressure and high-temperature conditions by chemical vapor deposition using high-cost Au-catalyst. Consequently, its applications as a crystalline semiconductor material in electronic devices are limited due to the low quality and purity of BP. In this work, we demonstrate an efficient and low-cost synthesis of highly crystalline BP by rapid low-pressure reaction of red phosphorus (RP) in the presence of a small amount of silver (Ag) in a vacuum-sealed quartz tube. The phosphorene layers were prepared by liquid-phase exfoliation (LPE) of high-quality BP crystals using various solvents such as isopropanol (IPA), N-methyl pyrrolidone (NMP) and Dimethylformamide (DMF). The resulting materials are investigated in detail including structural and morphological characterization along with thermal properties. We have obtained BP flakes which are uniform in size and morphology. The lateral sizes of the stable BP range from 50.7 nm after exfoliation in IPA to 204 nm after exfoliation in NMP. The most effective phosphorene layer separation was achieved by using the IPA solvent and centrifugation at 15000 rpm with a monolayer thickness of 0.5 - 0.6 nm. Phosphorene layer thicknesses of 1.0 - 2.0 nm and 1.7 – 2.6 nm are obtained when using NMP and DMF as solvents, respectively. We demonstrate the fine tuning of the optical bandgap by controlling the number of phosphorene layers.

**Keywords:** black phosphorus, low-pressure synthesis, liquid phase exfoliation, phosphorene layers, structural and morphological characterization.