Exfoliating thinner flakes of phosphorene at higher yield

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In the past two years, phosphorene has attracted increased attention due to its potential in thin, flexible electronics. And because it is naturally a semi-conductor, phosphorene holds promise where miracle material graphene falls short.

"There has been a decade-long attempt to make graphene semi-conducting," said Northwestern University's Mark Hersam. "Our group and others have tried to do it with limited success. So why not just use a material that is already a semi-conductor?"

In order for phosphorene to reach its full potential, it needs to be incredibly thin—preferably at the atomic scale. Until now, researchers have experienced difficulties in exfoliating atomically thin flakes from the bulk material, called black phosphorous, in a quick and efficient manner. Hersam, however, may have solved this problem. His group recently developed a method that results in substantially higher exfoliation yield and much thinner flakes than previous efforts.

Supported by the National Science Foundation and Office of Naval Research, the research is described online in the April 18 issue of *Proceedings of the National Academy of Sciences*. Joohoon Kang, a graduate student in Hersam's laboratory, is first author of the study.

After being exfoliated from black phosphorous, phosphorene has dramatically different electronic and mechanical properties from its parent material. Not only are the atomically thin, two-dimensional layers powerful semiconductors, but they also efficiently emit light, suggesting opportunities for optoelectronics.

"Graphene taught us that the most scalable method was to exfoliate in a solution," said Hersam, Walter P. Murphy Professor of Materials Science and Engineering at Northwestern's McCormick School of Engineering. "You begin with a solvent and then add graphite and a surfactant. After introducing energy via sonication, you can exfoliate the graphite down to graphene. It would seem obvious that the same approach would work with phosphorene. The difference, however, is that phosphorene is very reactive chemically, which requires important changes in protocol to achieve exfoliation without degradation."

When exposed to open air, the chemical reactivity of phosphorene leads to rapid deterioration. The result suggests that components of air, such as water and oxygen, are driving degradation and need to be avoided. Consequently, Hersam initially bypassed this issue by exfoliating with organic solvents in a closed, air-free and water-free environment.

"The problem with the organic solvent approach is that it is very inefficient," he said. "It results in low exfoliation yield and flakes that are relatively thick."

The breakthrough came when Hersam and his team realized—after a year of studying the degradation process—that phosphorene degrades in the presence of both water and oxygen together. By bubbling an inert gas through water, Hersam deoxygenated it to create an aqueous solvent for exfoliating black phosphorous that avoids degradation. After sonicating black phosphorous in a mixture of deoxygenated water and surfactants, he found substantially higher exfoliation yield and much thinner flakes that reached the atomically thin limit.

In addition to providing superior phosphorene materials, the method uses commonly available, environmentally benign water as opposed to organic solvents.

"We took the resulting exfoliated flakes and fabricated transistors out of them," Hersam said. "The device metrics were among the best reported for any exfoliated phosphorene, thereby confirming that we had isolated high quality material in a scalable manner without degradation."

More information: Stable aqueous dispersions of optically and electronically active phosphorene, Joohoon Kang, DOI: 10.1073/pnas.1602215113

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