

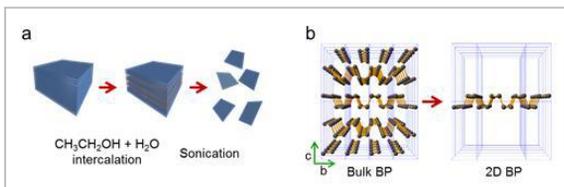
## 흑린 반도체 박막 대량생산 기반 마련

• 교신저자 : 이현욱, 이주한(환경·소재)

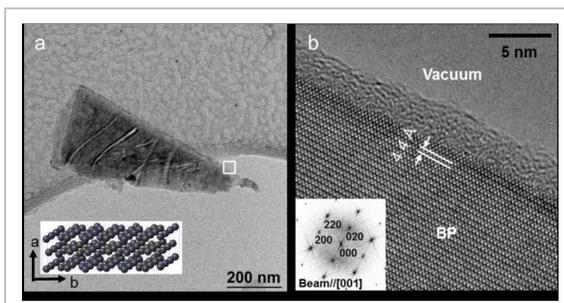
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### 연구내용

액상박리법을 이용하여 세계 최초로 흑린 덩어리에서 결정성 높은 원자층 단위 박막을 얻는데 성공함. 기존과 달리 에탄올과 물을 사용하는 간단한 액상 박리법을 이용하여 결정성 높고 질 좋은 흑린 박막을 얻는 방법을 제시하였으며, 실제 전자 소자 제작에 바로 응용이 가능하다는 것을 보여줌. 특히 이론적 계산과 모델링을 통해 삼각형 형태의 박리와 에너지간의 관계를 규명하는 과학적 근거를 제시하여 질적으로 우수한 박막을 대량 생산할 기반을 구축함. 또한 흑린 박막으로 트랜지스터를 제작하여 특성을 조사한 결과, 아세톤을 선택적으로 감지할 수 있음을 발견하여 향후 센서 등의 활용이 가능할 것으로 보임.



[그림 1] 에탄올과 물을 이용한 화학적 박리 방법을 통해 벌크 흑린에서 원자층으로 쪼개지는 과정을 형상화함.



[그림 2] 흑린의 고배율 투과 전자 현미경 이미지. 흑린이 벌크에서 원자층으로 쪼개질 때 에너지가 안정적인 면으로 쪼개지므로 삼각형 모양의 단결정 박막이 형성됨.

### 기대효과

흑린을 활용하여 실제 소자 제작이 가능한 실용화 단계로 발전할 연구기반을 마련하였으며, 이 기술을 통해 흑린 박막의 다양한 응용소자를 개발할 수 있게 됨.

## SCIENTIFIC REPORTS

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### Triangular Black Phosphorus Atomic Layers by Liquid Exfoliation

Soonjoo Seo<sup>1</sup>, Hyun Uk Lee<sup>1</sup>, Soon Chang Lee<sup>1</sup>, Yooseok Kim<sup>1</sup>, Hyeran Kim<sup>1</sup>, Junhyeok Bang<sup>1</sup>, Jonghan Won<sup>1</sup>, Youngjun Kim<sup>1</sup>, Byoungnam Park<sup>1</sup> & Joughahn Lee<sup>1</sup>

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Few-layer black phosphorus (BP) is the most promising material among the two-dimensional materials due to its layered structure and the excellent semiconductor properties. Currently, thin BP atomic layers are obtained mostly by mechanical exfoliation of bulk BP, which limits applications in thin-film based electronics due to a scaling process. Here we report highly crystalline few-layer black phosphorus thin films produced by liquid exfoliation. We demonstrate that the liquid-exfoliated BP forms a triangular crystalline structure on SiC<sub>2</sub>/Si (001) and amorphous carbon. The highly crystalline BP layers are faceted with a preferred orientation of the (010) plane on the sharp edge, which is an energetically most favorable facet according to the density functional theory calculations. Our results can be useful in understanding the triangular BP structure for large-area applications in electronic devices using two-dimensional materials. The sensitivity and selectivity of liquid-exfoliated BP to gas vapor demonstrate great potential for practical applications as sensors.

The increasing demand for elemental 2D materials, such as graphene and transition metal dichalcogenides (TMDCs), emerged for applications in sensors<sup>1</sup>, optoelectronics<sup>2,3</sup>, flexible displays<sup>4</sup>, and photovoltaics<sup>5,6</sup>. Although graphene has high carrier mobility<sup>7</sup>, its zero band gap limits various electronic applications<sup>8</sup>. Recent studies found that phosphorene, monolayer of black phosphorus, can be mechanically exfoliated similarly to graphene<sup>9,10</sup>. Contrary to graphene, black phosphorus (BP) has a band gap of 0.3–2 eV, which allows it to be exploited as an excellent semiconductor and potentially an alternative for graphene<sup>11–13</sup>. In addition, we reported that BP can be applied to produce highly efficient photoanodes<sup>14,15</sup>. Previous studies on the electronic applications of BP<sup>16,17</sup> are based on the layer-dependent nature of BP<sup>18,19</sup>. Bulk BP layers are stacked together by the van der Waals force and can be easily peeled off layer by layer<sup>20</sup>. Most of the recent studies on BP are based on mechanically exfoliated BP bulk samples<sup>21</sup>. Although mechanical exfoliation is an effective technique to cleave bulk materials into mono or few layers, it is limited by a scaling process. Therefore, it is necessary to employ a liquid method for large scale and various practical applications. Previous work proved that BP deposited on SiC<sub>2</sub>/Si by the liquid exfoliation forms high-quality single crystalline nanoflakes<sup>22</sup>. Brent *et al.* reported that few-layer phosphorene was produced by liquid exfoliation of BP in *N*-methyl-2-pyrrolidone<sup>23</sup>. Other studies on BP layers by liquid exfoliation showed that BP atomic layers look like debris or flakes with a random shape or orientation<sup>24</sup>. None of them, however, showed well-defined crystalline thin films covering whole substrates. Hence, they appear to be inappropriate for thin film based electronic applications.

Our liquid exfoliation method uses higher sonication energies than the conventional method and different solutions, as illustrated in Fig. 1a, which allows us to obtain highly crystalline triangle-shaped BP thin films. Unlike the liquid exfoliated BP flakes with random shapes reported in the literature, our BP sample cleaves into faceted triangular atomic layers, similar to triangle-shaped flakes commonly observed in MoS<sub>2</sub> nanocrystals<sup>25–28</sup>. The thickness and the density of BP layers on the substrate can be easily changed by adjusting the sonic energy and the concentration of BP in our sample. Using our method, it is possible to produce ultrathin BP films varying in thickness from monolayers to few layers. It can be challenging to design uniform thin films using BP flakes with random shapes because high coverage of BP is needed to uniformly cover the whole substrate, which results in thick stacked BP layers close to bulk BP. The fabrication of nano devices using single BP flakes has been

<sup>1</sup>Advanced Nano-surface Research Group, Korea Basic Science Institute, Daejeon, 34133, Republic of Korea. <sup>2</sup>Department of Applied Chemistry and Biological Engineering, Chungnam National University, Daejeon, 34134, Republic of Korea. <sup>3</sup>Spin Engineering Physics Team, Korea Basic Science Institute, Daejeon, 34133, Republic of Korea. <sup>4</sup>Department of Materials Science and Engineering, Hongik University, Seoul, 04066, Republic of Korea. Correspondence and requests for materials should be addressed to U.L. (email: leeuk@kbsi.re.kr) or J.L. (email: joughahn@kbsi.re.kr)