Synthesis and Lithium Battery Applications of Few-layer Black Phosphorous (BP) Nanosheets

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Advantages of BP

- Layer-dependent direct bandgap
  - Bulk to monolayer: 0.3 – 1.0 eV
- Semiconductor-metal transition
  - Deformation-induced
Advantages of BP

- High carrier mobility
  \(~1000 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}\)
- High On/off Ratio
  \(~10^5\)
Potential Applications of BP

Gas sensor
Singlet oxygen generator
Photodetector

Radio-frequency transistors
Memory device
Organic photovoltaics

H. T. Yuan et al., Nat. Nanotechnol. 2015, 10, 8, 707.
Disadvantages of BP

Bad stability!

- Oxidized in air
- Decompose at ~400 °C
Stability of BP

Prevent oxidization

Surface coating

Surface modification

Utilize oxidization

For single-layer BP

Neuromorphic synaptic device

J. D. Wood et al., *Nano Lett.* 2014, 14, 12, 6964.
Synthesis of Few-layer BP Film

X. S. Li et al., 2D Mater. 2015, 2, 031002.

Thin BP film on PET

Problems:

- Very thick
  ~ 40 nm
- Not uniform
  rough surface
- Low quality
  polycrystalline

No effective way to obtain large-area, high-quality monolayer BP film!
Another Way Out

Thick flakes, at 50 mA g\(^{-1}\)

Large powders, at 24 mA g\(^{-1}\)

- Low conductivity
- Severe volume expansion
- Small work current density
- Fast capacity decay

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific capacity (mAh g(^{-1}))</th>
<th>Conductivity (S m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>372</td>
<td>(\sim 10^8)</td>
</tr>
<tr>
<td>BP</td>
<td>2596</td>
<td>(\sim 10^2)</td>
</tr>
<tr>
<td>Si</td>
<td>4200</td>
<td>(\sim 10^{-4})</td>
</tr>
</tbody>
</table>

M. Nagao et al., *J. Power Sources* 2011, 196, 6902.
## Synthesis of Bulk BP

### Comparison of Present Methods

<table>
<thead>
<tr>
<th>Methods</th>
<th>High Temp. high Press.</th>
<th>Bi/Hg catalyst</th>
<th>HEMM</th>
<th>Sono-chemistry</th>
<th>Gas-phase transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials</td>
<td>white P</td>
<td>white P Hg/Bi</td>
<td>red P</td>
<td>red P</td>
<td>red P, SnI₄, AuSn</td>
</tr>
<tr>
<td>Conditions</td>
<td>p &gt;10000 atm</td>
<td>normal pressure</td>
<td>ambient Ar</td>
<td>sonication</td>
<td>vacuum</td>
</tr>
<tr>
<td>Size</td>
<td>mm-scale</td>
<td>5x0.1x0.07 mm²</td>
<td>nm-scale</td>
<td>tens of um</td>
<td>cm-scale</td>
</tr>
<tr>
<td>Time</td>
<td>tens of min</td>
<td>tens of hours</td>
<td>tens of hours</td>
<td>several hours</td>
<td>several hours</td>
</tr>
<tr>
<td>Quality</td>
<td>high</td>
<td>low</td>
<td>low</td>
<td>high</td>
<td>very high</td>
</tr>
</tbody>
</table>

- Toxic chemicals
- Complex apparatuses
- Small size
- Time-consuming

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Characterization of Bulk BP

Large size

High purity

XRD

Raman

High-crystallinity

Exfoliation of Few-layer BP Nanosheets

<table>
<thead>
<tr>
<th>Solvent</th>
<th>NMP</th>
<th>DMSO</th>
<th>CHP</th>
<th>DMF</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>b. p. (°C)</td>
<td>204</td>
<td>189</td>
<td>154</td>
<td>153</td>
<td>100</td>
</tr>
</tbody>
</table>

Quality of Few-layer BP Nanosheets

**Evidences**

**XRD:** only more new peaks appear, no new phases introduced

**Raman:** $A_g^1/A_g^2 > 0.6$, pristine BP

**XPS:** almost no oxides exist
Structure of Few-layer BP Nanosheets

High-quality, clean surface
BP-G Hybrid Paper Electrode

G : BP = 20 : 80 wt%

BP nanosheets wrapped by G flakes, effectively confining the expansion of BP nanosheets during charge/discharge cycles.

High flexibility
Electrochemical Behaviors

- Lower overpotential
- Better rate capability
- Higher specific capacity
- 402 mAh g$^{-1}$ after 500 cycles
BP Nanoparticle-G Hybrid Electrode

G : BP = 20 : 80 wt%
Agglomeration of BP nanoparticles leads to weak interaction with G flakes, impossible for performance test
Broken when peeling off
Application for Lithium-sulfur Battery

- Higher energy density
- Abundant resources
- Low conductivity
- Polysulfide “shuttle effect”
- Growth of Li dendrites
- Volume expansion

Performance related

Safety related

Density Functional Theory Calculation

FLP nanosheets act as polysulfide immobilizer, reducing loss of capacity and keeping integrity of structure.
FLP-CNF Electrode

Cross-section

Inner part

CNF: carbon nanofiber  FLP: few-layer phosphorene

FLP : CNF ~15 : 85 wt%  highly flexible

FLP nanosheets uniformly distributed in CNF matrix

Morphology of Electrodes

Before cycling

Cathode with FLP fasten polysulfide

Anode in battery with FLP nanosheets keep intact

After cycling

Anode

Cathode
Cyclic Voltammetry (CV)

FLP-CNF

CNF

Peak potentials

Onset potentials

FLP nanosheets act as catalyst, accelerating reaction

Higher reduction peak and lower oxidation peak potentials
Galvanostatic Charge/discharge Tests

Promoted specific capacity
After 500 cycles, 660 mAh g$^{-1}$ remains, coulombic efficiency ~98%

Better rate capability
Conclusions

- High-quality few-Layer BP nanosheets have been prepared by exfoliation in water.

- Using of graphene in BP-G hybrid paper promoted the conductivity of electrode and confined expansion of BP.

- Adding small amount of BP into CNF electrode greatly improves overall performance due to the catalyst effect and its role as polysulfide immobilizer.
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Thank you for your attention!