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Continuos-Flow Synthesis of High-Quality Few-Layer Antimonene Hexagons

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Background

A novel family of layered materials from group-15 of the Periodic Table, called Pnictogens (P, As, Sb and Bi) have gained increasing attention due to their semiconducting behavior, with thickness-dependent band gaps that can be modulated by strain, doping, or chemical functionalization, which can be useful for fabricating optoelectronic devices. Additionally, these **2D-Pnictogens** offer unique photonic, catalytic, magnetic, and electronic properties. [1] Within this chemical group, black phosphorous shows bandgap thickness-dependency but its use is hampered because of its high reactivity with ambient water and oxygen. Alternatively, **antimonene**, another 2D-Pnictogen, seems to be an excellent candidate exhibiting interesting theoretically-predicted properties. However, only a few of them have already been experimentally demonstrated, while many others remain a challenge due to the absence of a suitable synthetic method to produce the required high-quality material. [2] Antimonene can be isolated using top-down and bottom-up approaches. On the one hand, top-down methods such as micromechanical exfoliation has demonstrated the ability to give rise antimonene monolayers with limited lateral dimensions and poor yields. Another physical method, base on liquid-phase exfoliation, has been demonstrated the ability to produce non-well-defined and partially oxidized hexagonal antimonene nanoflakes. [3] On the other hand, bottom-up methods based on sublimation and on-surface deposition, as well as molecular beam and van der Waals epitaxy approaches, have been developed to provide high-quality antimonene flakes but are not suitable for large-scale synthesis. [4] Along this front, another bottom-up approach has been recently reported, involving a solution-phase synthesis of well-defined hexagonal few-layer antimonene via anisotropic growth. [5] Nevertheless, this **colloidal approach** is limited to a batch-to-batch synthesis and low yields.

Motivation

Optimization of the synthetic parameters of the colloidal synthesis of few-layer antimonene hexagons and **up-scaling** of this process using a **continuous-flow synthesis (CFS)** that allow the production of **large quantities of high-quality antimonene flakes** to pave the way for their **incorporation in optoelectronic devices.**

Results and Discussion

Optimized Batch-to-Batch Synthesis

$SbCl_3$-DDT solution

0.914 g (4 mmol) of SbCl3+ 4 mL Dodecanethiol (DDT) + 6 mL 1-Octadecene (ODE)

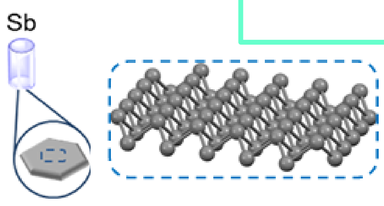
Vacuum overnight at 110º C

2 h under Ar at 150º C

Keep at 60º C under Ar

Antimonene nanosheets reaction

4 mL Octadecene + 0.5 mL Oleylamine
Hot injection of 1 mL of $SbCl_3$-DDT solution followed by:
•10 s of reaction a 300 ºC and cool down with dry ice.
•0 s of reaction at 300 ºC and cool down at room temperature.
Centrifuge and washing with $CHCl_3$



Continuous-Flow Synthesis

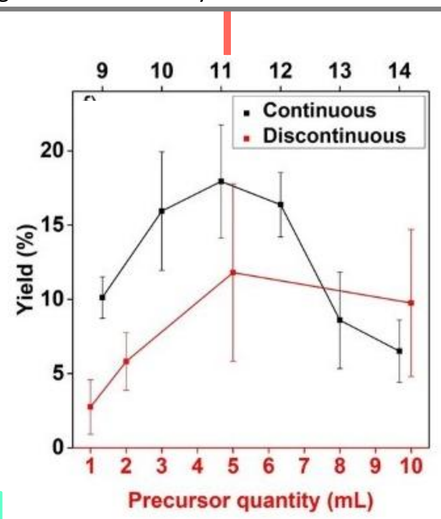
Precursor + reaction medium

Antimonene nanosheets

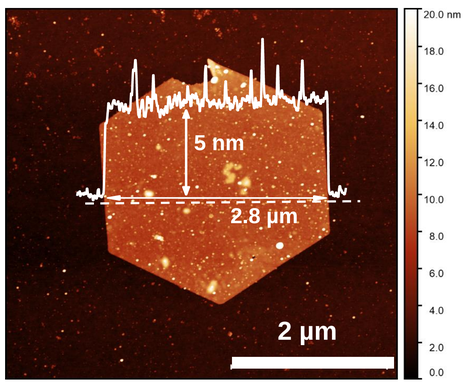
In the continuous synthesis, we do not use the hot injection method, but instead, the precursor and reaction medium are mixed at 30 °C before introducing the mixture in the reactor. This modification directly affects the reaction temperature, which decreases from 300 °C used in the hot injection method to 250 °C .

Yield Comparison batch-to-batch vs. CFS

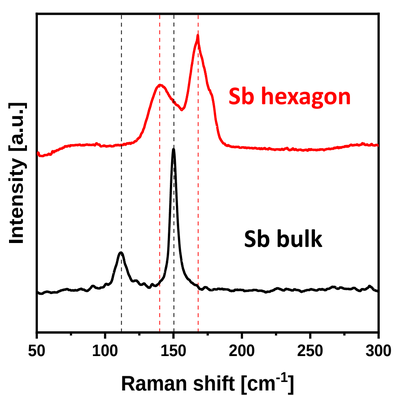
CFS gives rise to a maximum **yield closes to 18 %**, at 11 mL·min^{-1}, which is significantly higher than the best yield obtained with the **batch method (12 %)**.



AFM



Raman



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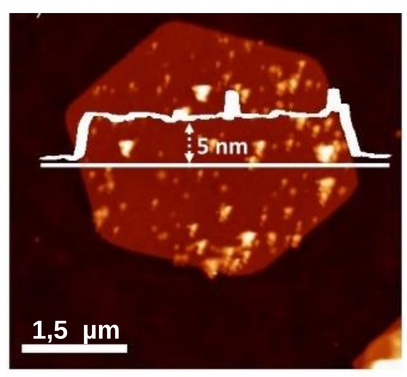
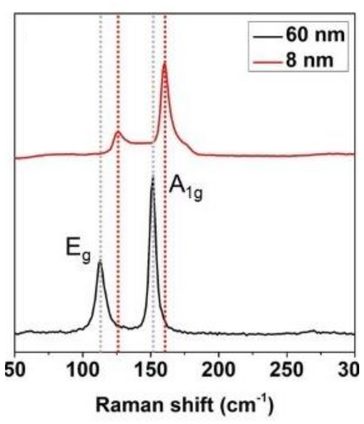


Raman



AFM picture (left) and **Raman** (right) picture of a pure and thin Sb hexagonal nanosheet obtained by **batch-to-batch synthesis.**

AFM picture (left) and **Raman** (right) picture of a pure and thin Sb hexagonal nanosheet obtained by **continuous-flow synthesis.**

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