

## Synthesis and Physicochemical Properties of Two-Dimensional Gallium Sulfide Crystals

Chuanfang John Zhang<sup>1,2\*</sup>, Xinhua Liu<sup>4</sup> and Valeria Nicolosi<sup>1,2,3\*</sup>

<sup>1</sup> Centre for Research on Adaptive Nanostructures and Nanodevices (Crann) & Advanced Materials Bio-Engineering Research Centre (Amber), Trinity College Dublin, Dublin 2, Ireland

<sup>2</sup> School of Chemistry, Trinity College Dublin, Dublin 2, Ireland

<sup>3</sup> School of Physics, Trinity College Dublin, Dublin 2, Ireland

<sup>4</sup> Department of Chemistry, Tongji University, Shanghai, China

\*Corresponding authors: Zhang CJ, Centre for Research on Adaptive Nanostructures and Nanodevices (Crann) & Advanced Materials Bio-Engineering Research Centre (Amber), Trinity College Dublin, Dublin 2, Ireland, Tel: +353-(0)1-896-4837; E-mail: zhangjc@tcd.ie

Nicolosi V, Centre for Research on Adaptive Nanostructures and Nanodevices (Crann) & Advanced Materials Bio-Engineering Research Centre (Amber), Trinity College Dublin, Dublin 2, Ireland, Tel: + 353 (0)1 896 4480; E-mail: nicolov@tcd.ie

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### Abstract

Two-dimensional (2D) materials possess exotic properties and have been received huge research interests. The group III-VI semiconducting nanosheets (NS) in particular, have been viewed as promising candidates for ultrathin and flexible optoelectronic devices and also for energy storage device. Liquid-phase exfoliation (LPE) could scalably synthesize 2D NS with good quality but in a much lower cost. This mini-review has briefly summarized the recent synthesis and application of 2D NS, with focuses on the LPE approach and fabrication of 2D NS/carbon conductive composite. The future electrochemical studies of 2D NS/carbon composite for Li-ion batteries anode has also been proposed.

**Keywords** Two-dimensional; Nanosheet; Liquid-phase exfoliation; Lithium-ion battery, Composite

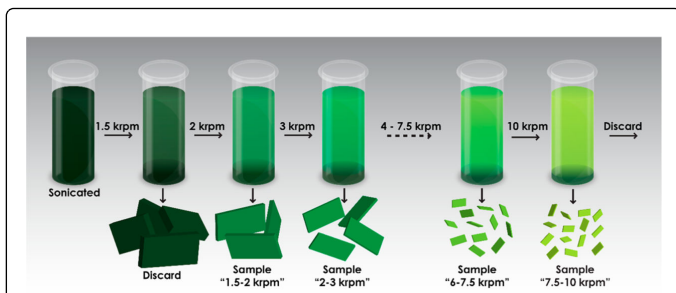
(SiO<sub>2</sub>/Si plate) and flexible (polyethylene terephthalate) substrates, yielding superior photoresponsivities of conducting broad band photodetection from 450 to 785 nm.

### Introduction

Recently, two-dimensional (2D) materials have attracted huge research attention due to their exotic properties [1-4]. 2D materials, such as MoS<sub>2</sub>, [5,6] WSe<sub>2</sub>, [7] stack as thin layered crystals, intriguing huge research ranging from sensing [8,9] to energy applications [10]. In addition to them, the group III-VI semiconducting nanosheets (NS) in particular, have been viewed as promising candidates for ultrathin and flexible optoelectronic devices and also for energy storage device [11-13]. For example, layered metal chalcogenides (MC, M=Ga, In, Ta; C=S, Se, Te) NS exhibit remarkable mechanical, thermal, anisotropic optical and electronic advantages [14-16].

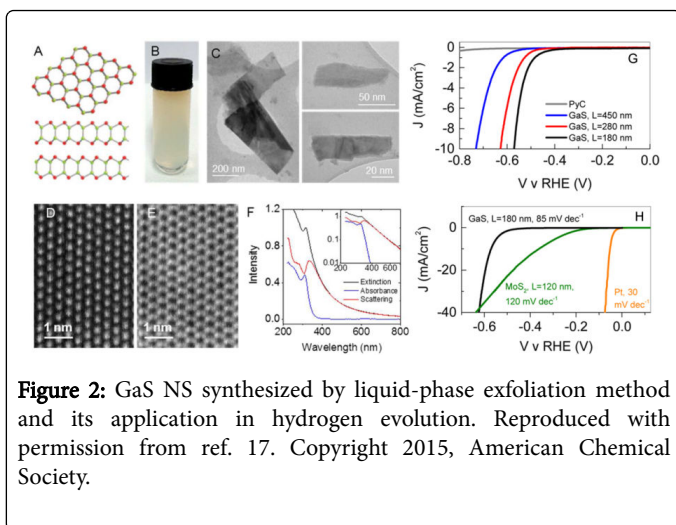
Pioneering work on the synthesis and properties of these MC NS have been reported over the past few years [17,18]. Late et al. [19] reported the 2D single-sheet GaS and GaSe transistors via a micromechanical cleavage technique, demonstrating excellent electron differential mobility. Hu et al. [20] obtained ultrathin GaSe NS by mechanical cleavage-solvent exfoliation method, which demonstrated fast response, high responsivity and quantum efficiency in photodetectors. The layered GaSe NS can also be used as a Li-ion battery (LiB) anode [21]. Liu et al. [22] reported multilayer GaTe flakes which exhibit a higher photoresponsivity than graphene, MoS<sub>2</sub>, and other layered compounds, showing promising applications in optoelectronic and photosensitive devices. 2D InSe ultrathin sheets have been reported as a promising candidate in optoelectronic devices, such as field-effect transistors and highly responsive photodetectors [23]. Tamalampudi et al. [18] fabricated few-layered InSe on rigid

It's worth mentioning that any of these applications requires large amount of MC NS, rendering the necessity of scalable production of MC NS. Typically, the layered semiconducting crystals are held together by weak van der Waals forces. One could overcome this force by applying the sonic energy to the crystals, either via bath or tip sonication, to obtain MC NS in large quantities with few-layer enriched dispersion. Such a process also termed as "liquid phase exfoliation", which possesses clear advantages over the traditional mechanical/chemical exfoliation approaches [16,24]. Moreover, the NS size could be selected by controlled centrifugation of the exfoliated dispersion, as shown in Figure 1. This is important, as the size of NS strongly determines the optoelectronic properties [25].



**Figure 1:** Size selection mechanism using controlled centrifugation approach. Reproduced with permission from ref. 10. Copyright 2016, American Chemical Society.

As a representative member of the layered MC family, gallium sulfide, GaS, shows promising applications in photoelectronics and gas sensing [26,27]. The production of GaS NS is, however, limited by quantities and NS stability [28]. As indicated previously, physical exfoliation of layered GaS by micromechanical cleavage leads to low throughput [28]. On the other hand, chemical exfoliation would result in a quick NS degradation [29]. In 2015, Coleman et al. [24] obtained GaS NS by exfoliating the commercial crystals in a range of solvents, with GaS-NMP being the optimized system. The exfoliated GaS NS were further processed into electrodes for electrocatalysis application, whose performances strongly depend on the size of NS, as shown in Figure 2 [30].



**Figure 2:** GaS NS synthesized by liquid-phase exfoliation method and its application in hydrogen evolution. Reproduced with permission from ref. 17. Copyright 2015, American Chemical Society.

On the other hand, the multi-valence of Ga and S enables multiple charge-transfer reactions and high theoretical capacity as a LiB anode. The semiconducting nature of GaS could be compensated by adding conductive agents, such as carbon onions, carbon nanotubes, graphene, etc. Ding Q et al. [29] deposited GaSx thin films onto single-walled carbon nanotubes (SWCNT) using an atomic deposition method. The discharge capacity of the composite reached 575 mAh g<sup>-1</sup> per electrode and 770 mAh g<sup>-1</sup> per GaSx at 120 mA g<sup>-1</sup>. On the other hand, the GaS/conductive composite could explore the high theoretical capacity of GaS, fast electron transport paths of the conductive network and high ionic conductivity in the 2D NS and porous nanostructure, possibly rendering the composite with high capacities and excellent rate capabilities.

We also note that, it is important to clarify the electrochemical reactions by gaining a more thorough understanding during charge/discharge process. For example, by conducting in-situ X-ray diffraction (XRD) we are able to observe the formation of new phases and their reversibility during charge/discharge, and correlate to the electrochemical kinetics. High-resolution transmission electron microscopy (TEM) would also be necessary for directly observation of new crystals post cycling. In doing so, we are able to define the sources of the high capacity, either from Li<sup>+</sup> intercalation, or from conversion, or alloying process.

Clearly, the GaS NS/conductive composite represents only one combination of Ga, S and conductive agent. Actually, various combinations, such as GaSe, GaTe, InSe NS based composite could be easily fabricated. The compositions, electrode thickness and NS size of the electrode could be easily controlled to maximize the specific capacities and optoelectronic properties. Such an exciting materials configuration and nanostructure certainly deserves further investigation.

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