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Organic–inorganic hybrid ZnS(butylamine) nanosheets and their transformation to porous ZnS

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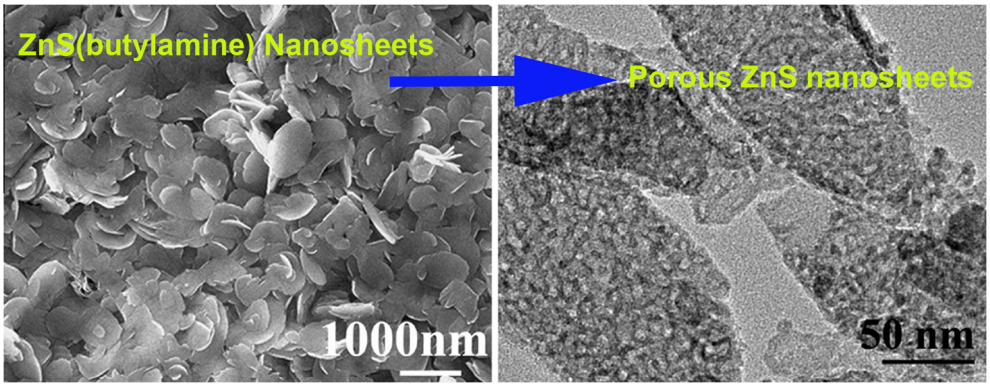
GRAPHICAL ABSTRACT



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ABSTRACT

Two-dimensional (2D) nanosheets possess the very essential features of nanomaterials, including quantum-confinement effects and unconventional reactivity, and are of special interest for a variety of promising applications. Here we report a facile chemical transformation strategy to prepare porous ZnS nanosheets *via* the organic–inorganic hybrid ZnS(butylamine) nanosheet-like precursor prepared from zinc diethyldithiocarbamate. The hybrid ZnS(butylamine) precursor show unique nanosheet-like structure composed by ZnS nanocluster region and non-crystalline region. The ZnS nanoclusters with crystallized state show the same crystal orientation in the nanosheets. A simple calcination process in nitrogen can induce the transformation of ZnS(butylamine) hybrid precursor to porous ZnS nanosheets. Different calcination temperature will cause the formation of porous ZnS nanosheets with different microstructure. In addition, the photoelectrochemical properties of the ZnS-based products including ZnS(butylamine) and porous ZnS nanosheets were investigated. This organic–inorganic hybrid precursor strategy to porous sulfides would also be suitable for fabricating other metal chalcogenides.

1. Introduction

Recent development on the synthesis and fabrication of two-dimensional (2D) nanosheets with thin thickness has created a new way to systematically tune optical and electronic properties

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of various functional materials, simply by manipulating physical dimensions. 2D nanosheets, especially the so-called "ultrathin nanosheets", have attracted extensive attention from scientists [1–8,9]. The nanosheets with smaller thickness can not only enhance the intrinsic properties of their corresponding bulk samples, but also may give birth to totally new functions [10,11]. In addition, the outstanding performance and processability of these 2D nanosheets makes them promising building blocks for a wide range of applications. For 2D nanosheets, the typical material is graphene or N-doped graphene [12,13].

The past few years have witnessed great progress in producing the ultrathin nanosheets [14,15]. Despite the remarkable success, the synthesis of different kinds of ultrathin nanosheets remains a great challenge. Up to now, there are two categories to synthesize 2D nanosheets: (1) Various exfoliation strategies [16–22], including gas molecules assisted exfoliation, substitutional-solid-solution based exfoliation, chemical etching assisted exfoliation, lithium intercalation-deintercalation exfoliation, and lamellar hybrid intermediate based exfoliation. There are lots of advantages of liquid exfoliation method, for example, being facile to control and economic. While, the exfoliation strategy often suffers relatively low exfoliation efficiency and wide range of thickness for exfoliated nanosheets. (2) Direct chemical synthetic strategies, including solution-phase growth, vapor deposition, and multilayer assemblies [23–26]. Solution-phase methods such as solvothermal or colloidal growth reactions offer a facile production method to synthesize gram scale quantities of 2D nanosheets with precise thickness [27–29]. With the above two routes, some 2D nanomaterials including ultrathin metal chalcogenide compounds such as ZnSe [30], SnSe [31], and SnS [32,33] have been synthesized in solution phase and demonstrated unique electronic structures and physical properties compared to their bulk forms. For example, Lee et al. reported the scalable synthesis of SnS nanosheets on N-reduced graphene sheet and found that the sheet-like composite shows enhanced electrochemical activity with long-term stability in various media [33].

Recent years, a unique type of II–VI semiconductor–amine hybrid materials have been synthesized on a large scale through facile solution phase reactions [34–36]. These II–VI semiconductor-based organic–inorganic hybrid materials often show enhanced optical and catalytic properties due to the synergistic effect between semiconductors and amines composition. It is believed that the amine composition in the material provides unique microstructure for the hybrid compound and modulates the interfacial charge transfer behavior, which induces the enhanced properties. For example, the hybrid material of $ZnSe{\cdot}0.5N_2H_4$ performs much better in the photodegradation of rhodamine B than the two counterpart products [37]. Li et al. demonstrated that the $Zn_{2-2x}Cd_{2x}S_2$(*n*-hexylamine) hybrid compounds exhibit enhanced emission intensity of white light than that of the inorganic counterpart [38]. In addition, these II–VI semiconductor-based organic–inorganic hybrid materials can be used as efficient intermediates to prepare inorganic chalcogenide nanostructures. For examples, with $ZnS(piperazine)_{0.5}$ hybrid materials, Jang et al. prepared N-doped ZnS nanoparticles [39]. Hyeon and coworkers have successfully prepared 1.4 nm thick CdSe nanosheets through a CdSe–amine hybrid complex [40]. $ZnS(en)_{0.5}$ (en = ethylenediamine) organic–inorganic hybrid material was also used to be a precursor for synthesis of sheet-like ZnS through thermal decomposition [41]. Recently, Zhang et al. reported the synthesis of ultrathin CdS nanosheets with lamellar CdS–DETA hybrid nanosheets as starting materials [42]. Due to the usual lamellar-like structures formed in II–VI semiconductor–amine hybrid materials, they are potential precursors for synthesis of 2D nanosheets.

As an important wide band-gap semiconductor, ZnS has been extensively studied due to its superior properties and wide applications in infrared windows [43], sensors [44], light-emitting diodes (LEDs) [45,46], and photocatalysis [47]. Although the synthesis of ZnS materials with different morphologies, such as 0D [48,49] and 1D [50,51] micro-/nanostructure, has widely been reported, controlled synthesis of high quality 2D ZnS-based nanosheets with thin thickness and porous ZnS nanosheets by a facile way still remains a great challenge.

Herein, we present a solvothermal route to prepare colloidal organic–inorganic hybrid ZnS(amine) nanosheets with zinc diethyldithiocarbamate ($Zn(ddtc)_2$) as Zn and S source. It was found that the reaction temperature, time, and kinds of amines highly influences the morphology and size of the hybrid ZnS (amine) nanosheets. Interestingly, the ZnS(amine) nanosheets are composed by ZnS nanocluster region and non-crystalline region. The ZnS nanocluster with crystallized state showed the same crystal orientation in the nanosheets. Through a simple calcination process ZnS(amine) nanosheets can be transformed into pure porous ZnS nanosheets. In addition, the photoelectrochemical properties of the ZnS-based products including ZnS(butylamine) and porous ZnS were also investigated.

2. Experimental section

2.1. Materials

All chemical regents were used as received without further purification. Sodium diethyldithiocarbamate ($Na(S_2CNEt_2)$), $ZnSO_4{\cdot}7H_2O$, methanol, ethanol, *n*-butylamine, *n*-propylamine, 1-dodecylamine, *iso*-propamide, phenylamine, and oleyl amine employed in this research are A.R. grade and were purchased from Sinopharm Chemical Reagent Co. China. Deionized water was used in all the experiments. Fluorine-doped SnO_2 coated glass substrates (FTO) were purchased from Wuhan lattice solar energy technology Co., LTD.

2.2. Synthesis of $[Zn(ddtc)_2]$ ($ddtc = S_2CNEt_2$) precursor

$Zn(ddtc)_2$ was prepared based on a previously published procedure [52]. In a typical synthesis, $Na(S_2CNEt_2)$ (20 mmol) was dissolved in 40 mL of methanol. $ZnSO_4{\cdot}7H_2O$ (10 mmol) was dissolved in 40 mL of deionized water. $ZnSO_4$ aqueous solution was then drop-wisely added into $Na(S_2CNEt_2)$ solution. The obtained mixture was stirred vigorously for at least 1 h. The formed white solid product, $Zn(ddtc)_2$, was then separated by filtration, washed at least for three times with deionized water followed by drying.

2.3. Synthesis of ZnS(butylamine) nanosheets and porous ZnS nanosheets

The ZnS(butylamine) nanosheets were synthesized by a solvothermal method. In a typical procedure, 0.08 g $Zn(ddtc)_2$ were firstly dissolved in 1 mL of chloroform; and then 10 mL of *n*-butylamine was added. After vigorously stirring, the obtained mixture was added into a 30 mL of Teflon-lined stainless steel autoclave, which was heated at 60 °C for 10 h and allowed to cool to room temperature naturally. The obtained precipitate was separated by centrifugation, washed with ethanol for several times, and dried in vacuum for further analysis.

For removing the organic composition in the product, the obtained ZnS(butylamine) nanosheets were calcinated in nitrogen atmosphere at 200–400 °C for 30 min with a heating rate of 2 °C/min. With this calcination route, ZnS(butylamine) nanosheets were transformed into porous ZnS nanosheets.