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Short communication

Two-dimensional (2D) amorphous antimony (III) trisulfide nanosheets: Synthesis, photoelectronic property and their transformation to crystalline 1D micro/nanorods

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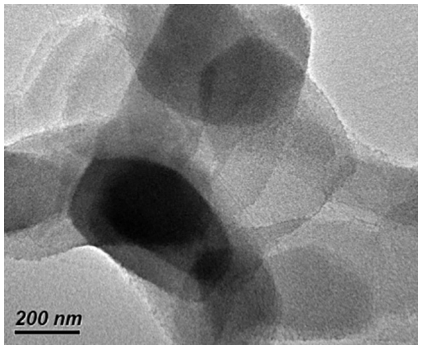
GRAPHICAL ABSTRACT



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ABSTRACT

Two-dimensional (2D) crystal materials have attracted intensive research interest because of their multifunctionality. However, the 2D nanosheets (NSs) of amorphous semiconductors are far less explored. We demonstrate here the colloidal synthesis of 2D amorphous antimony (III) trisulfide (Sb_2S_3) NSs in the mixture solution of different long-chain primary amines. These organic amines act as soft template to define the 2D growth through the coordination of metal cations with amine group. The resultant NSs exhibit distinct 2D characteristic with the thickness of 2–4 nm and the length × width dimensions ranging from several hundreds of nanometer to one to several micrometers. Their photoelectronic property has been evaluated in the indium tin oxide (ITO)/Sb_2S_3/ITO model device, showing fast temporal photoresponse and photoswitch ability. Through a solid-state thermal-annealing process, the amorphous NSs can be converted to 1D crystalline micro/nanorods, which is due to the high structural anisotropy of crystal phase (stibnite). TG-DSC thermal analysis reveals that the amorphous-crystalline phase transformation is companied by the desorption and/or decomposition of organic surfactant molecules and the S loss.

Antimony (III) trisulfide (Sb_2S_3) has been actively studied in thin-film solar cells [1–5], photodetectors [6,7], lithium/sodium ion batteries [8–10], and photocatalysis and other applications [11,12]. In crystallography, Sb_2S_3 displays two forms of amorphous (a-Sb_2S_3) and crystalline (c-Sb_2S_3) states: the former is usually prepared at low temperatures while the latter obtained at relatively high temperatures; they show different structural, optical, and (photo)electronic properties [1,4,8,13–16]. As an amorphous semiconductor, a-Sb_2S_3 is structurally

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isotropic, showing the long-range disorder (short-range order) structure [14,17]. Consequently, the morphology of a-Sb_2S_3 is easily dependent on its growth environment. For example, the thin films of a-Sb_2S_3 could be deposited on planar substrates (e.g., quartz glass or ITO/glass) [4,5,11,13,15,17]; as far as individual particles are concerned, the spherical grains of a-Sb_2S_3 (in powder samples or thin films) [18,19] were produced from solution-phase synthesis due to the thermodynamic energy minimization. In the past decade, the two-dimensional (2D) materials, such as graphene, MoS_2, g-C_3N_4, and $M(OH)_x$, have been intensively investigated because of their various functions and applications [20–23]. To our best of knowledge, however, the 2D solids of a-Sb_2S_3 have not been reported.

Amorphous semiconductors with the 2D feature, such as ultrathin nanosheets (NSs), may show great potential in (photo)electronic devices and energy applications. Amorphous a-Sb_2S_3, compared to its crystalline phase, has been found to show better electrochemical properties in rechargeable lithium batteries [8], such as high energy density, long cyclability and good initial Coulombic efficiency. These electrochemical properties would be probably further improved when ultrathin a-Sb_2S_3 NSs are accessed. Moreover, it is believed that the 2D NSs of amorphous semiconductors can exhibit specific (photo)electronic performances that are different from 2D crystal materials when used in the (photo)electronic devices based on individual NSs [20,21]. As such, the studies on the synthesis and (photo)electronic properties of 2D amorphous semiconductors are of much interest and scientific significance.

Herein, we introduced the synthesis of 2D amorphous Sb_2S_3 NSs via a simple colloidal chemistry method. Organic long-chain primary amines, oleylamine (OLA) mixed with n-dodecylamine (DA) or n-octylamine (OA), were employed as soft template [24,25] to assist the 2D formation of amorphous NSs. Their morphology, dimensional sizes, structure and chemical compositions were characterized in detail; their photoelectronic response behaviour was evaluated as active material in the indium tin oxide (ITO)/Sb_2S_3/ITO device structure. Moreover, these 2D amorphous Sb_2S_3 NSs can be transformed to 1D crystalline micro/nanorods by simple solid-state thermal-annealing, during which it is considered that the 2D to 1D morphology transition is driven by the high anisotropy of crystal structure of c-Sb_2S_3 (stibnite).

Amorphous a-Sb_2S_3 NSs were synthesized at relatively low temperatures through a colloidal chemistry method we reported recently [26]. The mixture of oleylamine (OLA) with n-dodecylamine (DA, n-$C_{12}H_{25}NH_2$) or n-octylamine (OA, n-$C_8H_{17}NH_2$) were employed as colloidal reaction solution (see details of experiments in the Supplementary material). The as-prepared sample was characterized by XRD pattern (Fig. 1a). No sharp peaks were detected, indicating the lack of long range order and the amorphous (non-crystalline) characteristic of Sb_2S_3 sample. Both the broadened peaks and the orange colour are indicative of the yield of amorphous Sb_2S_3 (a-Sb_2S_3) [15,16]. By simple thermal annealing, the orange a-Sb_2S_3 sample can transfer to crystalline Sb_2S_3 (c-Sb_2S_3), which has a dark or even black colour and stibnite structure (Fig. 1a, discussed in detail later). SEM and TEM studies (Fig. 1b–e) show that the a-Sb_2S_3 products display a two-dimensional (2D) sheet-like morphology. As revealed by EDS analysis, these a-Sb_2S_3 NSs have a Sb/S composition close to the theoretical stoichiometry of 2:3 (Fig. S1). The electron diffraction (ED) and HRTEM results are shown in Fig. 1f, in which only diffraction halo is observed and no lattice fringes are detectable, further verifying the non-crystalline nature of a-Sb_2S_3 NSs.

From the TEM images, it is seen that the length and width of a-Sb_2S_3 NSs are larger than the thickness and they both have a relatively large size, approximately ranging from several hundreds of nanometers to one to several micrometers. The NS thickness was determined by AFM imaging. As displayed in Fig. 2, these NSs show 2–4 nm in thickness. The thickness is much thinner than the length and width, unambiguously confirming the 2D geometric characteristics of a-Sb_2S_3 NSs.

XPS was used to characterize the chemical composition and elemental valent states of a-Sb_2S_3 NSs. In the XPS survey spectrum (Fig. 3a), only Sb, S and C is detected, indicating the high purity of sample (C signal comes from the C standard reference with 284.4 eV). From the high-resolution Sb 3d and S 2p spectra displayed in Fig. 3b and c, it is measured that Sb $3d_{5/2}$ and $3d_{3/2}$ have the binding energies of 529.3 and 538.7 eV, respectively, in good agreement with the trivalent Sb 3d core values from Sb—S bonds and precluding Sb—O species [4,26,27]; the binding energies S $2p_{3/2}$ and $2p_{1/2}$ correspond to 161.1 and 162.2 eV. As is known, XPS is a powerful tool to probe the surface chemical composition. For the a-Sb_2S_3 NSs, the Sb/S molar ration obtained from XPS results is very close to 2:3 (inset of Fig. 3a), which is consistent with the composition of bulk a-Sb_2S_3.

Organic long-chain primary amines, such as oleylamine (OLA), octadecylamine (ODA, n-$C_{18}H_{37}NH_2$), n-dodecylamine (DA, n-$C_{12}H_{25}NH_2$), and n-octylamine (OA, n-$C_8H_{17}NH_2$), have been often used to prepare 2D crystal materials [24,25,28]. As proposed in the literature, all these amines are able to serve as soft templates through the interaction between metal cations and –NH_2 groups and yield the ultrathin sheet-like morphology, like the formation of 2D CdSe NSs [24], ZnS nanobelts [25], and In_2S_3 NSs [28]. Similarly, the production of amorphous a-Sb_2S_3 NSs can be attributed to the soft template effect of mixed long-chain OLA and DA. As an amorphous (non-crystalline) solid, a-Sb_2S_3 lacks the long-range order in the atomic arrangements and is free of the limit of structural anisotropy, unlike many crystalline solids. The shape of a-Sb_2S_3 individual nanoparticles is highly related to their external synthetic conditions and formation mechanisms. Accordingly, the 2D template effect derived from the metal cations and –NH_2 groups is capable of well defining the growth and formation of amorphous Sb_2S_3 NSs.

These a-Sb_2S_3 NSs obtained from the mixed solution of organic long-chain amines could be readily dispersed in nonpolar solvents, such as n-hexane, toluene and chloroform, and made into thin films on the ITO-coated glass substrate by the drop-cast method. Accordingly, a pristine optoelectronic device with the typical electrode/materials/electrode (electrode: conductive ITO or metal thin film) sandwiched structure [26,28] was fabricated for measuring the photoresponse performance of a-Sb_2S_3 NSs. Fig. 4a shows the *I–V* curve of such a device under both the dark and visible-light irradiation conditions. The linear characteristic of *I–V* curves indicates the Ohmic contact nature between the ITO electrode and the a-Sb_2S_3 NS film. Compared to the dark current, the photocurrent is obviously increased when the ITO/a-Sb_2S_3 NSs/ITO device is exposed to light. Meanwhile, these 2D a-Sb_2S_3 NSs show good temporal photoresponse ability and photoswitch characteristic with the light on/off, as confirmed in the *I–t* curve measurement (Fig. 4b). Such a photoresponse property suggests that these amorphous Sb_2S_3 NSs may be applied as a component material in photodetection and solar cells [1–7,16], if their photostability is further improved under light illumination.

TG-DSC thermal analysis technique was employed to determine the phase change process of as-prepared a-Sb_2S_3 NSs. As shown in Fig. 5, a fast weight loss starts at the temperature 226.5 °C with a weight loss ratio about 28% in the TG curve within the temperature range of 50–400 °C, while the DSC process shows an obvious endothermic peak centered at 239.7 °C. After such an annealing process in TG-DSC analysis or a similar annealing reaction performed in a conventional tube furnace, crystalline products were produced, which crystalize in the stibnite structure of Sb_2S_3 [1,4–6,8,13,15,29], as verified by XRD in Fig. 1a. Clearly, the amorphous a-Sb_2S_3 NSs undergo a crystallization process during the thermal annealing. According to the TG-DSC curve, the crystallization begins at 226.5 °C and the fastest rate of weight loss takes place at 239.7 °C. The measured amorphous-crystalline transition temperature (226.5 °C) is consistent with many previous reports wherein c-Sb_2S_3 thin films or nanostructures of good crystallinity were usually obtained at 200–300 °C or higher preparation temperatures via the solid-state annealing or reaction [1,4–7,13,15,16,19,29,30]. There