Site-controlled synthesis and mechanism of three-dimensional Mo$_2$S$_3$ flowers

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Abstract

High-density three-dimensional Mo$_2$S$_3$ flowers have been facilely synthesized with controlled sites by introducing gold particles to trigger the growth in a CVD process. Without gold particles, nanopetals could be observed under a very dense S concentration. While gold was introduced, dense products with flower-like morphology could be readily obtained in a wide range of S:MoO$_3$ molar ratio from 1:5 to 5:1. The morphology and structure of the as-synthesized nanostructures were characterized using field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HRTEM). The growth mechanism was proposed in which gold particles acted as the initial nucleation sites fixing the nucleation position of the flowers following vapor–solid growth mechanism.

1. Introduction

Nanomaterials have attracted intensive research interest in the past decade for their novel structure and potential applications [1–4]. Recently, nanostructured metal chalcogenides have received particular attention. Among various metal chalcogenide nanostructures, nanostructured Mo$_2$S$_3$ have been extensively investigated due to their applications for electrode materials [5], electrochemical hydrogen storage [6] and optoelectronics [7]. Up to now, nanostructured Mo$_2$S$_3$ with different dimensions have been prepared including nanowires [8], nanotubes [9,10], flowers [11,12] and nanospheres [13] by various methods, such as chemical vapor deposition (CVD) [14], hydrothermal synthesis [15,16], template method [17,18] and sulfurization of MoO$_2$ [11]. The comprehensive investigation of Mo$_2$S$_3$ has also stimulated the research on the trivalent molybdenum sulfide, Mo$_2$S$_3$ [19–21]. Mo$_2$S$_3$ nanostructure can be either prepared by a solid–gas reaction between MoO$_3$/Al$_2$O$_3$ powders as the starting materials were loaded in ceramic boats, respectively, with the molar ratio varying from 1:5 to 5:1. The MoO$_3$ powders were placed at the center of the quartz tube, while the S powders were put at the entrance of the furnace, upstream of an Ar flow which acted as carrier gas. A commercial carbon paper (E-Tek) used as the substrate was put near the ceramic boat containing MoO$_3$ powders at the down stream of the Ar flow. Two kinds of carbon paper were used: one was plain carbon paper without any pre-treatment; the other one was pre-treated by depositing a very thin Au film on the surface. The quartz tube was purged by Ar flow prior to the synthesis. Then the furnace was heated up to the reaction temperature (810 °C), and kept for 2 h to make the starting materials react completely. Finally the furnace was cooled down to the room temperature.

The products collected from the surface of the carbon paper were investigated by field emission scanning electron microscopy...
3. Results and discussion

Fig. 1 shows SEM images of the typical Mo$_2$S$_3$ flowers synthesized with S:MoO$_3$ molar ratio of 1:1 in the starting materials on carbon paper with Au particles. Dense products were observed on the carbon fiber (Fig. 1a). The products feature three-dimensional flower-like morphology (Fig. 1b). The entire diameter of the nanoflowers is from 1.9 to 3.6 \( \mu \)m. Each flower consists of tens to hundreds of pieces of nanopetals (Fig. 1c). The nanopetals have very smooth surface and sharp edge, and are slightly curved (Fig. 1d). The nanopetals are from 500 nm to 2.3 \( \mu \)m in width and have extremely thin thickness of around 10 nm.

HRTEM images are shown in Fig. 2. Fig. 2a depicts that the nanopetals are a little curved and quite thin, which is consistent with SEM results. The HRTEM image (Fig. 2b) and fast Fourier transformation (FFT) diffraction pattern (inset of Fig. 2b) are from the same individual nanopetal and reveal the high crystallinity of the petal. The interplanar distance is measured of 0.24 nm and belongs to the plane (1 1 2) of Mo$_2$S$_3$. The FFT diffraction pattern can be indexed as (1 1 2) and (1 1 1) crystal planes of monoclinic Mo$_2$S$_3$ (JCPDS card no.: 81-2031).

To investigate the effects of precursor concentration and gold particles on the growth of the Mo$_2$S$_3$ nanopetals, the growth without and with gold particles was carried out using different molar ratio of S:MoO$_3$ varied from 1:5 to 5:1 in the starting materials. The results of the growth without gold particles are shown in Fig. 3. With quite a small S:MoO$_3$ molar ratio of 1:5, many tiny particles and quite a few nanopetals were observed on the surface of carbon substrate (Fig. 3a and b). The size of nanopetals is from 450 nm to 1.5 \( \mu \)m in width and about 40 nm in thickness. By increasing the S:MoO$_3$ ratio to 1:1, bundles of small flowers appeared (Fig. 3c). The small flowers compose of very tiny petals with sharp edge and approximately 3 \( \mu \)m in the width (Fig. 3d). However, the amount of bundles of flowers is quite small, and most of the surface of the substrate is exposed. Keeping increasing the S:MoO$_3$ ratio to 5:1, the carbon substrate was completely covered by dense nanopetals (Fig. 3e). These nanopetals with sharp edge and thin thickness around several nanometers are quite dense and close-packed. The size of nanopetal is in a wide range from 500 nm to 3.2 \( \mu \)m in width.
Fig. 3. SEM images of the as-synthesized nanostructures without Au particles. (a) and (b) for S/MoO$_3$ molar ratio of 1:5; (c) and (d) for S/MoO$_3$ molar ratio of 1:1; (e) and (f) for S/MoO$_3$ molar ratio of 5:1.

(Fig. 3f). The above results indicate that the growth of nanostructure is affected by the concentration of S vapor. Concentrated S atmosphere can induce the growth of dense nanopetals and increasing the concentration of S could enhance the growth of the nanostructures.

On the other hand, aiming at controlled nucleation and growth of the flowers, a thin Au film could be introduced into the system since Au is a very popular catalyst in the growth of nanostructures [23–29]. A very thin Au film was deposited on the surface of carbon paper and all other experimental parameters were kept the same. SEM observation shows that the Au film is actually exhibited as well-dispersed Au particles with the diameter around 12–26 nm (Supplementary Fig. S1).

Fig. 4 shows the SEM images of nanostructures synthesized in the presence of Au at different S:MoO$_3$ molar ratio from 1:5 to 5:1. With the Au particles, though at relatively low concentration of S (S:MoO$_3$ molar ratio of 1:5), quite a big amount of nanopetals grew on the substrate shown in Fig. 4a. The nanopetals are very big from 600 nm to 4 $\mu$m in width and around 10 nm in thickness, and show sharp edge and smooth surface (Fig. 4b). Increasing the S:MoO$_3$ ratio to 1:1, dense nanopetals were close-packed and formed many flowers on the surface of carbon substrate (Fig. 4c). The size of these flowers is from 1.9 to 3.6 $\mu$m. Each flower composes of many petals and presents a three-dimensional morphology with an open structure which provides a huge specific surface (Fig. 4d). All the petals of the flowers have an extremely thin thickness, sharp edge and very smooth and clean surface. However, if the S:MoO$_3$ ratio was further increased to 5:1, the growth of nanostructure was influenced by the dense S atmosphere. The products still remain the nanopetal shape with the similar size but low density, and are not close-packed (Fig. 4e). Some of the petals are bent and not clean at the surface. There are many very tiny pieces of cracks as impurities decorated at the surface of nanopetals (Fig. 4f). Many particles which are another source of impurities are also observed at the roots and among the nanopetals.

By comparing the results with and without Au particles, the effect of Au is revealed. Without Au, dense nanopetals are only obtained in a very dense S atmosphere (S:MoO$_3$ ratio of 5:1). However, after introducing Au into the system, dense nanopetals and flowers can be steadily generated in a wide range of S:MoO$_3$ ratio from 1:5 to 5:1, which indicates that Au plays a very important role in the growth of the nanostructure. To investigate the effect of Au on the growth of nanostructure, the growth mechanism has been studied and proposed.

Scrutiny of the product morphology by SEM and TEM indicates that no melting behavior of the gold particles was observed, implying that the growth followed vapor–solid (VS) mechanism [30] instead of the so-called vapor–liquid–solid (VLS) mode [26,27]. The
growth mechanisms of the nanostructure with and without Au are similar, but the presence of Au makes it easier to trigger the growth.

Without the assistance of Au on the carbon substrate, at the beginning of the reaction, S (melting point: 115 °C) and MoO$_3$ (melting point: 795 °C) are evaporated and react in the vapor phase (Fig. 5a). MoO$_3$ is sulfided into Mo$_2$S$_3$ and transported to the carbon substrate by Ar carrier gas (Fig. 5b). The Mo$_2$S$_3$ precursors deposit on the surface of the plain carbon substrate and nucleate randomly depending on the surface conditions of the substrate. Then the continuous deposition of precursors happens at the surface of initial nuclei and the nuclei grow into big nanopetals and flowers following the VS mode[30]. In a VS mode, the amount of initial nuclei determines the growth density of nanostructures: more initial nuclei which provide more growth sites will result in denser products. However, the dense products are only obtained in highly concentrated S atmosphere (S:MoO$_3$ ratio of 5:1) which leads to the complete reaction between the starting materials and provides enough Mo$_2$S$_3$ precursors for the growth. That indicates without the assistance of Au the S concentration plays an important role in the nucleation and growth of the nanostructures. In the concentrated S atmosphere, high supersaturation of reactive precursors facilitates the formation of dense nuclei (Fig. 5f). The nuclei finally grow into big nanopetals and flowers (Fig. 5g and h). While at relatively low S concentration, nucleation only randomly occurs at some inhomogeneous sites of the bare carbon substrate which merely generates sparse nuclei (Fig. 5c and Supplementary Fig. S2), leading to a low density of final products (Fig. 5d).

On the other hand, when a very thin Au film is introduced, a large amount of Au particles can form on the surface of the substrate (Fig. 5e and Supplementary Fig. S1). These Au particles act as the initial growth sites at which the precursors are much easier to deposit at various S:MoO$_3$ ratios (Fig. 5f and Supplementary Fig. S3). Usually Au can be used to grow some novel nanostructures, like nanowires, in a VLS mode[26,27]. In the typical VLS mode, firstly Au particles absorb and alloy with the gaseous starting materials. When the Au particles are liquefied and supersaturated with the materials, the materials will precipitate and form nanostructures[27]. However, it is quite difficult to yield Au–S alloy due to the high volatilization of S and no melting behavior of the gold particles was observed as mentioned above[31]. Thus the growth of Mo$_2$S$_3$ nanopetals and flowers with Au particles is not a VLS process. We think Au particles here provide a low surface–energy interface and act as preferential sites for adsorbing Mo and S gaseous precursors, thereby facilitating the reaction of the starting materials and the nucleation and growth of Mo$_2$S$_3$ nanostructures [32]. Due to layered structure of Mo$_2$S$_3$, the dangling bonds on the edges of the initial sulfide nuclei can incorporate atoms directly from the gaseous precursors while the surface of the petals keep smooth and unreactive, which favors
Fig. 5. A schematic growth mechanism of nanopetals and flowers with and without Au particles. (a) sulfurization of MoO₃ by S; (b) Deposition of Mo₂S₃ on plain carbon substrate; (c) less Mo₂S₃ nuclei at low S concentration; (d) less and small nanopetals growing on plain carbon substrate at low S concentration; (e) carbon substrate with Au particles forming at the surface; (f) uniform and dense Mo₂S₃ nuclei forming at the carbon substrate; (g) and (h) Mo₂S₃ nuclei growing into dense nanopetals and flowers.

lateral growth of the nanopetals and the architecture of flowers are finally obtained (Fig. 5g, h and Supplementary Fig. S4). Owing to the assistance of Au particles, the precursors are easily collected for the following nucleation in a wide S concentration range, and site-controlled growth of the flowers is realized based on VS growth mechanism (Fig. 5e–h).

4. Conclusions

Site-controlled growth of three-dimensional Mo₂S₃ flowers was realized with the assistance of Au particles in optimal concentrated S atmosphere in a CVD process. The effects of S concentration and Au particles were investigated. Without the assistance of Au particles, only high concentration S atmosphere can lead to the enhanced growth of the nanostructures. In the presence of Au particles, the growth of nanostructures is very easily triggered even in a wide range of S:MoO₃ molar ratio from 1:5 to 5:1. At the optimal S:MoO₃ ratio of 1:1, a big amount of flowers were obtained on the surface of the carbon substrate. The stable synthesis of high-density three-dimensional Mo₂S₃ flowers makes it possible for the applications in producing different nanodevices such as electrode materials for lithium-ion battery and field emission applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2012.09.070.

References