Materials Letters 166 (2016) 116–120

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Hierarchical α-MnS microspheres: Solvothermal synthesis and growth mechanism

Kezhen Qi [a], Rengaraj Selvaraj [b,*], Tharaya Al Fahdi [b], Salma Al-Kindy [b], Younghun Kim [c], Cheuk-Wai Tai [d], Mika Sillanpää [e]

[a] College of Chemistry and Life Science, Shenyang Normal University, Shenyang 110034, China
[b] Department of Chemistry, College of Science, Sultan Qaboos University, Muscat, Oman
[c] Department of Chemical Engineering, Kwangwoon University, Seoul 139-701, Korea
[d] Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden
[e] Laboratory of Green Chemistry, LUT Savo Sustainable Technologies, Lappeenranta University of Technology, Sammonkatu 12, FI-50130 Mikkeli, Finland

ARTICLE INFO

Article history:
Received 14 October 2015
Received in revised form
6 December 2015
Accepted 10 December 2015
Available online 11 December 2015

Keywords:
Manganese sulfide
Solvothermal synthesis
Hierarchical nanostructure
Growth mechanism

ABSTRACT

Hierarchical-like α-MnS microspheres have been successfully synthesized via a simple solvothermal route using L-Cystein as both sulfur source and capping agent. X-ray diffraction (XRD) analysis confirmed that these hierarchical microspheres were made of α-phase MnS. Morphological studies performed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods showed that the α-MnS hierarchical microspheres are obtained from the nanocubes by self-assembly due to the main driving force of the minimization of overall surface energy. It is highly expected this research can provide a useful fundamental understanding of shape-controlled synthesis of the semiconductor material with hierarchical microstructures.

1. Introduction

In recent years, hierarchical micro-/nanostructured materials have attracted considerable attention because of their unique shape-dependent properties, which significantly differ from or even do not exist in those of bulk or discrete counterparts [1–3]. These properties depend not only on their phase but also depend on their size, morphology, and arrangement that give the additional degrees of freedom to tailor the properties of the materials [4–6]. Thus, controllable synthesis of hierarchical architectures is of great interest and urgently called for. Up to now, scientists have been devoting considerable efforts to fabricate three dimensional (3D) hierarchical architectures assembled by the low dimensional nanoscale building blocks, such as nanoplates [7], nanoparticles [8], nanorods [9], and so forth [10]. However, it still remains to be a major challenge to develop a simple method to prepare hierarchical nanostructures with desired morphologies to obtain their new properties and exploring their promising applications.

Manganese sulfide (MnS) is an important semiconductor material that has been demonstrated to be of wide applications in magnetic [11], optical [12], optoelectronic [13] and luminescent fields [14]. It is well known that MnS has three different crystal structures: stable α-MnS, metastable β-MnS and γ-MnS structures. Both tetrahedrally coordinated β-MnS and γ-MnS forms are easily transformed into octahedrally coordinated α-MnS forms at high temperature [15]. Inspired by promising applications, great effort has been devoted to the synthesis of MnS nanocrystals with various morphologies and controllable crystalline phases. To date, a variety of novel shapes of MnS nanocrystals have been successfully synthesized, such as rods [16], spheres [17], cubes [18], stars [19], corals [20], flowers [21], bipods [22], boxes [23], dandelion [24], multipods [25], and so on. However, the efficient synthesis of MnS hierarchical structures by low-dimensional structure self-assembly using a simple method still remains a great challenge.

Herein, we present a facile solvothermal method for the synthesis of MnS hierarchical microspheres assembled by nanocubes using L-Cystein as both a sulfur source and a capping agent. The effect of L-Cystein on the morphology of MnS hierarchitectures and their possible formation mechanism were also discussed based on the experimental results. It is highly expected that this method would be extended to the shape-controlled synthesis of other semiconductor materials with hierarchical nano/microstructures.

* Corresponding author.
E-mail address: srengaraj1971@yahoo.com (R. Selvaraj).

http://dx.doi.org/10.1016/j.matlet.2015.12.044
0167-577X/

2. Experimental section

2.1. Preparation of MnS hierarchical microsphere

The MnS samples were synthesized using analytical grade manganese acetate ($C_4H_6MnO_4 \cdot 4H_2O$) and L-Cystein ($C_3H_7NO_2S$), without further purification. In a typical synthesis, 4.08 mmol of $C_4H_6MnO_4$ and 8.16 mmol of $C_3H_7NO_2S$ were dissolved in 70 mL of ethylenediammine and continuously stirred for 30 min to form a clear solution. Then, the above solution was transferred to an autoclave and heated at 180 °C for 10 h. The autoclave was taken out and allowed to cool naturally to room temperature. The as-prepared product was separated by centrifugation, washed several times with deionized water and ethanol, respectively, and then dried in an oven at 70 °C for 24 h.

2.2. Characterization of MnS crystals

The XRD patterns of the products were collected on a Bruker (D5005) X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å). An accelerating voltage of 40 kV and emission current of 30 mA were adopted for the measurements. The morphology were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL JEM-3010). X-ray photoelectron spectroscopy (XPS) was examined by a Sigma Probe (ThermoVG, U. K.) using the source of Al Kα radiation (1.486 eV). The photoemitted electrons from the sample were analysed in a hemispherical energy analyzer at a pass energy of Ep = 20 eV. All spectra were obtained with an energy step of 0.1 eV and a dwell time of 50 ms. The local chemistry of the samples were examined by energy dispersive X-ray spectroscopy (EDX) performed in the field-emission scanning electron microscope.

3. Results and discussion

3.1. The morphology and crystal structure of the products

Fig. 1 shows the XRD pattern of the as-prepared product with a molar ratio of 1:1 ($C_4H_6MnO_4$ to $C_3H_7NO_2S$) after reaction for 10 h at 180 °C. The reflections in the diffraction pattern are indexed to the cubic phase of α-MnS (JCPDS card No. 72-1534). The obvious peaks are correspond to the (111), (200), (220), (311) and (222) planes of the α-MnS crystal. The strong and sharp diffraction peaks in the XRD pattern indicate that the as-prepared products are well crystallized. No peaks of impurities were detected, revealing the high purity of the as-synthesized products.

The composition of the as-prepared MnS hierarchical microspheres was further investigate by XPS (Fig. 2). The binding energies in the XPS spectrum were calibrated by using of C 1 s (284.6 eV). The survey XPS spectrum confirmed the presence of C, O, Mn, and S elements (Fig. 2a). The observed C peak was due to the carbon supporting film on the copper TEM grid, and the O peak was due to the absorption of oxygen on the sample surface. The XPS spectra of MnS sample was consistent with the typical

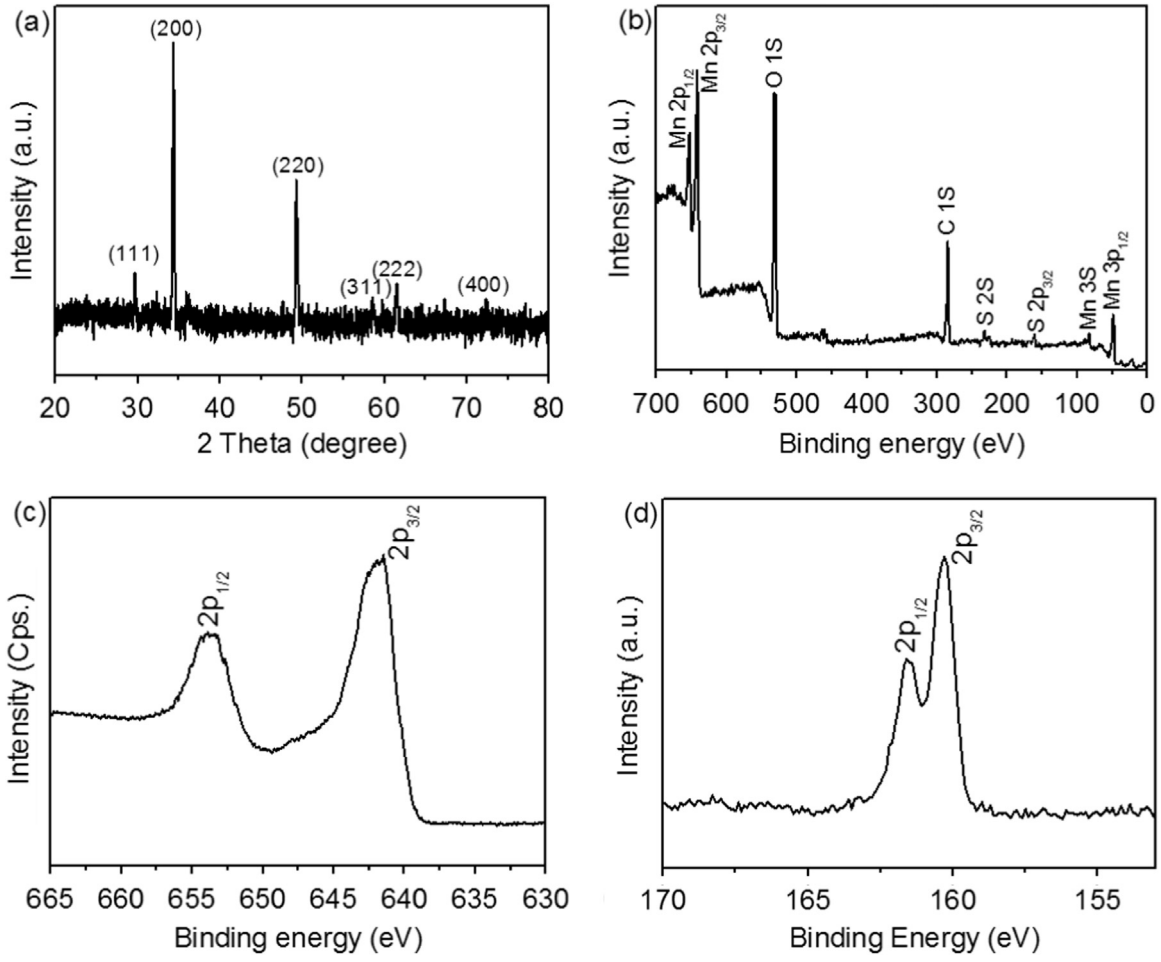

Fig. 1. Characterizations of as-prepared α-MnS microspheres: (a) XRD patterns; (b) XPS of the structures. High-resolution XPS analysis of the materials at the (c) Mn and (d) S regions is also presented.