FACILE SYNTHESIS AND CHARACTERIZATION OF FLOWER-LIKE MoS_2 MICROSPHERES

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Flower-like MoS_2 microspheres assembled by nanosheets have been successfully synthesized by a facile, environmentally friendly reaction in closed reactor at moderate temperature. The obtained products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The influences of reaction temperature and duration time were carefully investigated.

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1. Introduction

In the last decades, transition metal dichalcogenides MX2 (M = Mo, W, Nb and Ta, X = S, Se), which constitute a layered structure in analogy to graphite, have attracted great attention due to their striking properties and promising applications [1,2]. The layered structure is constructed by unit X-M-X atomic trilayers which the bonding between metal and chalcogens is covalent, and the trilayers themselves are held together by weak van der Waals forces [3,4]. The special layer-like structure results in numerous applications in hydrodesulfurization catalysis [5], electrochemical intercalation [6], solid lubrication [7–10], hydrogen storage [11], elastic and coating materials [12–14], and Li batteries [15, 16]. It is well known that properties of the materials are concerned with its size and shape. Compared with bulk materials, nanomaterials always show unique size- and shaped-dependent properties [17], and then controlled synthesis of nanoscale materials whose bulk counterparts show interesting behavior is critical for fundamental studies.

Molybdenum disulfide (MoS_2) is one of the transitionmetal dichalcogenide layered compounds, has been used for decades in specialised applications as a solid lubricant or an additive for lubricating oils and greases. Compared with ordinary MoS_2, nanoscale MoS_2 has more favorable properties such as much larger specific surface areas, strong absorbing ability, especially

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hydrodesulfurization (HDS) catalyzing ability [18]. Therefore, much effort has been devoted to the synthesis of various nanoscale MoS_2 with specific morphologies and unique properties. And many novel structures of MoS_2 have been obtained, including inorganic fullerene [19], nanoflowers [20], nanotubes [21,22], nanowires [23], nanorods [24] and core-shell structures [25].

However, MoS_2 hierarchical self-assembled nanostructures have rarely been reported, herein, we report the successful synthesis of flower-like MoS_2 microspheres via solid-state method. The products were characterized by X-ray powder diffraction (XRD), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The approach produced a high yield of structurally uniform nanostructures, which opens up possibilities for potential scalable applications. The growth mechanism of three-dimensional MoS2 microspheres is proposed on the basis of the experimental facts.

2. Experimental

2.1 Synthesis of MoS_2 samples

Elemental molybdenum and sulfur powders were purchased from Shanghai Chemical Reagent Co. Ltd. and used as received. In a typical preparation, a mixture of 1 g of Mo and 6.67 g of S was energetically ball-milled at 400 rpm (rotation per minute) in the presence of ethanol for 10 h in a planetary ball mill. Then ball-milled mixture was introduced into 10-ml stainless steel reactor in a nitrogen-filled glove box. The filled reactor is tightly closed with the threaded plug and pushed into the tube furnace. The temperature of tube furnace is raised to 850°C at a rate of 10°C /min and maintained at 850°C for 1 h in the atmosphere of N2. The closed reactor heated at 850°C is gradually cooled to room temperature and a black powder is obtained.

2.2 Characterization methods

The X-ray diffraction (XRD) patterns were recorded using a D8 advance (Bruker-AXS) diffractometer with Cu *Ka* radiation ($\lambda = 0.1546$ nm). The 2θ range used in the measurement was from 10 to 80° with a velocity of 5°/min. The morphologies and structures of the samples were characterized by scanning electron microscopy (SEM, JEOL JXA-840A) and transmission electron microscopy (TEM) with a Japan JEM-100CX II transmission electron microscope.

3. Results and discussion

3.1 Structure and morphology characterization

Molybdenum disulfide (MoS_2) microspheres with high purity were synthesized by solid-sate reaction method. The crystalline structure and phase purity of MoS_2 nanostructures were confirmed by XRD and EDS.As shown in Fig. 1a, All labelled diffraction peaks can be indexed to those of the pure hexagonal phase of MoS_2 with lattice constants a = 3.161 Å, c = 12.84 Å, which are in good agreement with the values of standard card (JCPDS No. 37-1492). No characteristic peaks were detected from other impurities, indicating that the sample was of high purity. Moreover, the XRD patterns reveal wide and weak diffraction peaks, which is evidence of the formation of small nanoparticles of the as-prepared MoS_2. The EDS result (Fig. 1b) demonstrates that the MoS_2 nanoflowers consist of only elements Mo and S, and no other elements was observed. Furthermore, the quantification of the peaks shows that the atom ratio of Mo: S is about 1:1.98, which is close to 1:2 by the atomic ratio of MoS_2. The size and morphology of MoS_2 samples were identified by SEM. Fig.1c shows that the obtained samples are uniform MoS_2 microspheres with an average diameter of about 1 μm. Fig.1d offers a clear view of the surface morphology which shows that the obtained MoS_2 microspheres are composed of many curly and interlaced nanosheets growing with wall thickness in the range of 19−23 nm in all directions. Fig.1e shows a typical TEM image of MoS_2 microspheres and reveals spherical structure of the obtained product, which agrees well with the SEM observation. More details for MoS_2 nanostructure are illustrated by HRTEM studies in Fig.1f, indicating that the nanosheets consist of about 10-layers structures. The distance between the lattice fringes is 0.63 nm, slightly larger than the reported data (0.62 nm) for the (002) planes of the hexagonal MoS_2 structure [26].

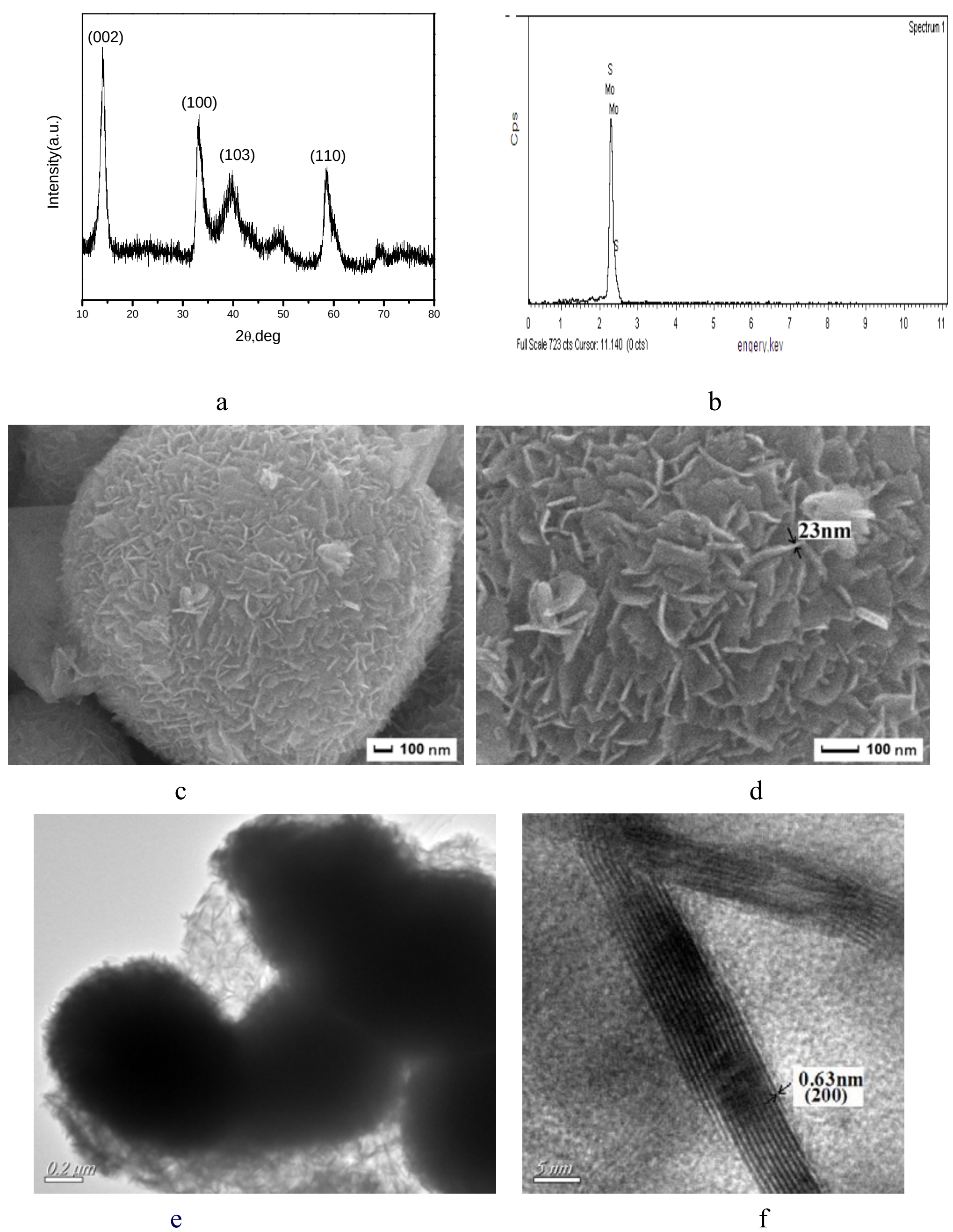

Fig. 1 XRD(a),EDS(b)SEM(c,d),TEM(e) and HRTEM (f) images of the as-prepared MoS_2 nanospheres

3.2 Influences of the reaction temperature

In order to study the growth process of 3D flower-like MoS_2 spheres, a series of experiments have been conducted. The influence of temperature on morphologies and structures was investigated from 400°C to 850°C. The XRD results and SEM images of the as-prepared samples were shown in Figs. 2 and 3, respectively. Fig. 2 shows typical XRD patterns of the samples obtained at 400°C, 500°C, 600°C, 700°C, 800°C and 850 °C. Combined with the XRD and SEM results, it was found that the products obtained at 400°C were mainly composed of Mo and MoS_2 with irregular shape (Fig 3a), indicated that Mo and S powders could not completely react at the lower temperature. With increasing the reaction temperatures to 500°C, the content of MoS_2 phase increased, and the obtained products were mainly composed of a large amount of bulks with the average size about 100 nm (Fig.3b). When the reaction temperature is further increased to 600°C, the product only contains MoS_2 phase, and the morphology changed from bulks to lamellas (Fig.3c). When the reaction temperature was further increased to 700°C, a large number of irregular lamella appeared and began to cluster together (Fig.3d). MoS_2 spherical structure composed of nanoparticles could be obtained and there were some small nanosheets scattered on the spherical surfaces at temperature of 800°C (Fig.3e). When the reaction temperature reached 850°C (Fig.3f), 3D flower-like MoS_2 micospheres with the diameter of about 1μm with nanosheets were obtained.

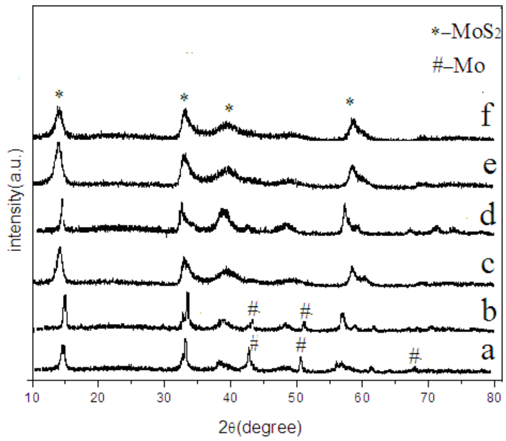

Fig.2. XRD patterns of the final products obtained at different temperatures:
a) 400°C, b) 500°C, c) 600°C, d) 700°C,e)800°C and f) 850°C (: MoS_2 peaks,#: Mo peaks).*

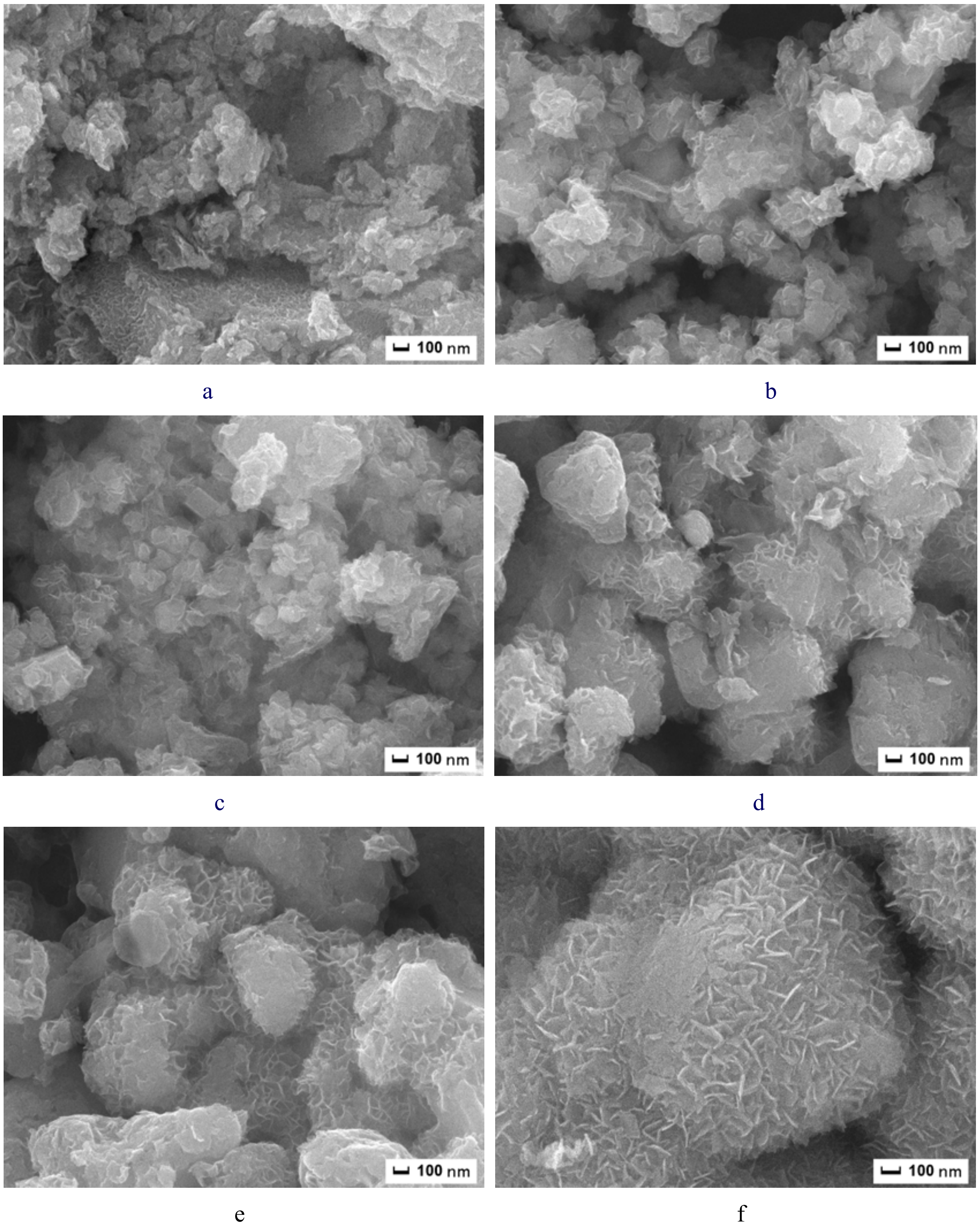

Fig. 3. SEM images of MoS_2 products obtained at different reaction temperatures: a) 400°C, b) 500°C, c) 600°C, d) 700°C, e) 800°C and f) 850°C

4. Conclusions

In summary, uniform 3D MoS_2 microspheres with an average diameter of 1 μm have been synthesized successfully via a facile solid-state reaction. The influences of the temperature on morphologies of the MoS_2 products were discussed. It is our hope that this efficient and simple synthetic route can be applied as a general method for the synthesis of other transitionmetal sulfide nano or micromaterials transition metal dichalcogenides.

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