FeWO₄/FeS core/shell nanorods fabricated by thermal evaporation

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1. Introduction

Hybrid systems combining two or more components open a new window for nanomaterials, improving their performances and expanding applications that are not available from their individual ones, among which core/shell nanostructures are an important option to combine multiple functionalities of materials in electronics, magnetism, optics, catalysis, electrochemistry, and so on [1,2]. For example, FeWO₄ is a p-type semiconductor, being able to present preeminent magnetic and optical properties [3] and possible to be applied in optical fiber and magnetic devices, but after deposited with carbon by a simple hydrothermal method, the obtained C-coated FeWO₄ composite would exhibit much better electrochemical cyclic performance than naked FeWO₄ [4]. FeS, which can be easily prepared by heating iron and sulfur in vacuum, has been of interest to energy industry in the catalytic processing of oil and gas [5], and can play an important role in biological systems (proteins and enzymes) acting as so-called active centers [6]; but when nanoscaled FeS was covered in multiwalled carbon shells by one-step thermal evaporation, the resultant FeS/C fibers would present ferromagnetic behavior [7], although FeS (troilite) itself is not ferromagnetic. Moreover, the FeS containing nanomaterials are still of a particular interest due to the existence of a huge number of spin configurations, which allow to use them in different devices in spintronics, magnetotronics, and so forth [6]. To our knowledge, however, core/shell structure composed of FeWO₄ and FeS has not been reported.

Moreover, most core/shell structures have been so far produced by chemical methods [2], in which the chemical reactions are complex and difficult to be controlled. On the contrary, physical vapor deposition, in particular thermal evaporation, is simple, controllable, flexible and reproducible, allowing synthesizing metal oxide nanostructures with good crystallization [8,9]. In this work, novel FeWO₄/FeS core/shell nanorods are prepared by thermal evaporation, in which both the core (FeWO₄) and shell (FeS) were well crystallized.

2. Experimental procedure

The reported products were synthesized by a high-temperature thermal evaporation process with a horizontal quartz tube furnace (for details on the setup, please check Ref. [10]). During an optimum processing, the evaporation sources, WO₃ and S powders, are loaded separately, in which a quartz boat with 1 g WO₃ powder was placed at the center of the furnace, while another boat with 0.01 g S powder was located at 14 cm apart from the WO₃ powder on the upstream of the furnace. Silicon wafers sputtered with approximately 5 nm of iron thin film were set at approximately 24 cm away from the WO₃ source on the downstream. Before heating, the quartz tube was evacuated and flushed repeatedly with Ar gas. Then the furnace was heated up to 1000 °C at a rate of 15 °C/min, and held there for 2 h. After that, the furnace was cooled naturally to room temperature at a rate of about 5 °C/min. The pressure inside the quartz tube was maintained at 500 mbar throughout the whole heating and cooling process. Finally, a blue-green layer of products was formed on the surface of the silicon substrate.

The as-synthesized products were characterized via field emission scanning electron microscopy (SEM, S4800), transmission
3. Results and discussion

Two typical SEM images of the products at different magnifications are displayed in Fig. 1, indicating that a large quantity of nanorods were grown on the substrate, and each individual nanorod has a uniform one-dimensional structure. By examining tens of the products, the calculated mean value of the diameter of the nanorods was 175 ± 60 nm, and that of the length was 1.4 ± 0.5 μm.

Further TEM observation revealed that the as-synthesized nanorods are of core/shell heterostructure, possessing a uniform layer of shell (light) coating on a uniform internal core (dark) (please see in Fig. 2a) under the presented optimum conditions. Through examining tens of nanorods, the calculated mean diameter of the core is approximately 160 ± 10 nm, and the thickness of the shell is about 8–25 nm (see in Fig. 2a and b). The recorded EDX spectrum of the nanorods as illustrated in Fig. 2c indicates that the core/shell nanorods are composed of W, O, Fe, and S. With the shell thickness reduced from 25 to 8 nm, the contents of W and O atoms increase from 11.0 to 18.87 at%, and 58.45 to 68.62 at%, respectively, but that of S atom is sharply reduced from 11.2 to 0.28 at% and Fe from 19.32 to 12.21 at%. This result reveals that the core/shell nanorods are composed of Fe and S, and the core is of Fe, W and O.

A typical HRTEM image of the core/shell nanorods is shown in Fig. 2e, where the insets represent the SAED patterns of the core (up left) and shell (down right) of the nanorod, respectively. The HRTEM observation demonstrates an obvious interface between the core and shell. The spacings of the lattice planes of the cores calculated from SAED pattern are approximately 0.59 and 0.51 nm which can be indexed as those of the (0 1 0) and (0 0 1) planes of a monoclinic FeWO4 phase (JCPDS card no. 71-2390), respectively. In accordance with the calculated result from SAED pattern of the shell, the well-resolved periodic lattice fringe of the shell in HRTEM image indicates that the spacing of the observed lattice planes are approximately 0.52 nm, which is consistent with the interplanar distance of the (1 0 0) plane of monoclinic FeS (JCPDS card no. 37-0477).

A typical Raman spectrum of the prepared FeWO4/FeS core/shell nanorods is shown in Fig. 3. The sharp band at 873 cm⁻¹ is assigned to ν1 symmetric A_g mode of terminal WO2, while the band at 690 cm⁻¹ is interpreted as an antisymmetric bridging mode associated with tungstate chain. The ν3 antisymmetric stretching mode at 820 cm⁻¹, ν2 bending mode at 322 cm⁻¹ and ν4 bending mode at 300 cm⁻¹ are corresponding to the bands observed in tungsten anion. The band at 137 cm⁻¹, which is below 200 cm⁻¹, can be attributed to the lattice vibration. All the results are corresponding to the Raman spectrum of FeWO4 reported by Ruiz-Fuertes [11] which gave ν1 as 878 cm⁻¹; ν3 as 692 and 777 cm⁻¹; ν2 as 330 cm⁻¹ and ν4 as 299 cm⁻¹. In addition, the band at 214 cm⁻¹ is assigned to the asymmetric stretching mode of FeS as reported in Ref. [12].

It is reasonable that the obtained FeWO4/FeS core/shell nanorods were formed by the following chemical reactions. As the temperature increases, tungsten trioxide and sulfur begin to sublime from the quartz boat. When WO3 meets with FeO resulted possibly from the reaction of the metallic Fe thin film on the substrate with the residual oxygen in the system, FeWO4 forms [13].

\[
\begin{align*}
2\text{Fe} + \text{O}_2 & \rightarrow 2\text{FeO} \\
\text{FeO} + \text{WO}_3 & \rightarrow \text{FeWO}_4
\end{align*}
\]  

In addition, the S vapor will react with metallic Fe, forming FeS.

To explain the growth of nanorods, two commonly recognized mechanisms were proposed in literature: vapor–liquid–solid (VLS) and vapor–solid (VS). It was indicated that a liquid droplet is the sign of VLS mechanism for the growth of nanorods [14]. However, the microstructure observation of the prepared nanorods in our work revealed that there were no other particles at their tips or roots. So, it is possible that a VS mechanism was responsible for the growth of the FeWO4/FeS core/shell nanorods. At the beginning of the growth, the original iron film fragmented into relatively small particles, absorbing WO3 vapor and residual oxygen, and reacting with them to form FeWO4 nuclei. The initially formed FeWO4 nuclei were inclined to be bounded by (0 1 0) facets which are likely the lowest energy surfaces and could act as the seeds for further growth of the crystals along the direction of [0 1 0]. When more crystalline FeWO4 precipitated on the particles, FeWO4 nanorods were formed. After that, due to their high surface activation, the formed FeWO4 nanorods will serve as

![Fig. 1. Typical SEM images of the as-synthesized nanorods: (a) low magnification, and (b) high magnification.](image-url)
nuclei, facilitating the absorption of FeS preferentially on the edges of them and thus widening of the nanostructure also through a VS mechanism [15]. In addition, because several planes of FeWO₄ and FeS exhibit a good epitaxial relationship, a perfect single-crystal epitaxial growth of FeS layer along the [100] direction could happen on the surface of FeWO₄ nanorods, finally forming the core/shell heterostructure. Because the detailed morphology of nanorods is controlled by the diffusion rate and the surface migration of gas phase species, as the supersaturation, substrate temperature, and temperature gradient were optimized and kept unchanged, the crystalline nanorods (either the core or the shell) would grow with uniform diameter distribution along a specific crystal growth direction.

4. Conclusions

FeWO₄/FeS core/shell nanorods were fabricated by thermal evaporation of WO₃ and S powders at 1000 °C onto Si substrate sputtered with iron thin film in a tube furnace. The nanorods are
175 ± 60 nm in diameter and 1.4 ± 0.5 μm in length, and each individual nanorod is of uniform diameter and well-crystalline core/shell structure. The cores of the synthesized nanorods are monoclinic FeWO4 and the shells are monoclinic FeS. Raman analysis divulged the FeWO4 Raman active optical phonon modes, positioned at 873, 820, 690, 322 and 300 cm⁻¹, and FeS at 214 cm⁻¹. The cores of the nanorods were supposed to grow through VS mechanism, and the FeS layers were then coated onto them through epitaxial growth.

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References