MoO₃ Structures Transition from Nanoflowers to Nanorods and Their Sensing Performances

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Abstract

Morphology transformation and crystal growth strategies of metal oxide semiconductors are extensive studied in material science recently, because the morphology and crystallinity of the nanomaterial have significant effect on the physicochemical characteristics. However, understanding the morphology changes of α-MoO$_3$ induced by annealing temperature is still a challenge. Herein, the nanostructure transition of MoO$_3$ induced by calcined temperature has been investigated through XRD and SEM method. It can be found that crystallization is highly dependent on the annealing temperature. In addition, the MoO$_3$ nanoflowers can change into nanosheets at 500 ºC. Afterwards, the nanosheets turn into microrods, especially at 900 ºC due to the growth of MoO$_3$ crystal. On the other hand, MoO$_3$ is a traditional sensing material, which is sensitive to many volatile organic compounds. Thus, the sensing performances of various MoO$_3$ nanostructures were measured. Compared with MoO$_3$ nanoflowers and microrods, the MoO$_3$ nanosheets based sensor has excellent sensing performance towards ethanol, and the maximum gas response value is 8.06.

1. Introduction

In the past few decades, the development of nanotechnology and band gap engineering have created various exotic metal oxide semiconductor (MOS) nanostructures, which open up new perspectives for their exploitation, significantly creating the novel and fascinating devices [1–5]. Consequently, metal oxide semiconductors have attracted significant attention in recent years for their applications to the secondary cells, sensors, memories, photodetectors, field-effect transistors, and heavy metal etc. [6–12]. For example, the traditional semiconductors of MoO$_3$ [13], In$_2$O$_3$ [14], TiO$_2$ [15] and ZnO [16], owing to their useful features such as exotic electronic structure, well chemical stability, non-toxicity, rich optoelectronic properties, low cost, high surface-to volume ratio and considerable sensitivity at low temperatures, have been regarded as the attractive materials for the quantum dots sensitized solar cells, lighting emitting components, high frequency devices, and catalysts [17–20]. On the other hand, the above physicochemical characteristics strongly depend on their shape and size, as well as morphology and crystallinity [21, 22].

Besides, nanostructure transformation and crystal growth are very important to fabricate the optoelectronic devices with superior performances [23]. Specifically, nanostructure design strategies offer interesting and extensive ideas to validly synthesis favorable functional nanomaterials due to its distinct characteristics at the nanoscale. For example, ultrafine NiO nanoparticles were acquired in situ by the approach of converting three-dimensional (3D) metal boron organic polymer into one dimensional (1D) boron organic polymer nanorod array at room temperature [24]. In addition, the facile advance of MgO nanostructures at different annealing temperatures (from 300 to 900 ºC) was developed [25]. Moreover, crystal quality is one of the other important factors for optoelectronic device. Recently, Jang and his coworkers observed the homoepitaxial growth of nanowires with constant outer diameters on bulk materials [26]. Additionally, high performance photodetector based on p-type Cu$_{1-x}$Ni$_x$O films were
prepared, and the crystal quality, morphology, and grain size of Cu$_{1-x}$Ni$_x$O films can be manipulated by Ni doping [27]. Of course, crystal growth and its quality are known to be significantly influenced by the crystallization environment.

As a representative n-type semiconductor oxide material with an energy gap of about 3.2 eV, molybdenum oxide (MoO$_3$) has been extensively used in various devices such as sensors, lithium-ion batteries, and photodetectors due to the high thermal and chemical stability [28–30]. Owing to different experimental conditions, MoO$_3$ exhibits many nanostructures, for example, nanoribbons, nanosheets, nanowires, nanoflowers and nanorods [29–31]. Consequently, the research regarding MoO$_3$ nanostructure has gained popularity. However, the morphology transformation induced by annealing temperature is not yet well researched.

Herein, the MoO$_3$ nanostructure transformation and crystal quality induced by annealing temperature is more compelling. The crystalline MoO$_3$ was obtained from MoS$_2$ precursor calcined in the range of 400–900 ºC in air, respectively. The results show that the nanostructure can be manipulated from nanoflowers to nanorods via alteration of annealing temperature.

2. Experimental Section

2.1 Materials

Commercially available solvents and metal salts were used without further purification. Specifically, Ammonium molybdate ((NH$_4$)$_2$MoO$_4$), glucose (C$_6$H$_{12}$O$_6$), ammonium fluoride (NH$_4$F), Thiourea (CH$_4$N$_2$S), trimethylamine (C$_6$H$_{15}$N) were purchased commercially from Aladdin company, China.

2.2 Fabrication of MoO$_3$ materials

The flower-shaped MoS$_2$ was synthesized by hydrothermal processes similar to our previous study [28]. In a typical synthesis, 1.8 g ammonium molybdate, 1.8 g thiourea, 1 g glucose, firstly, to add 200 mg of ammonium fluoride into 50 mL distilled water, then triethylamine (200 µL) was dropped slowly with a pipette, and stirred vigorously for 30 min. Afterwards, the resulting mixtures were sealed in a 60 mL Teflon-lined stainless-steel autoclave and heated at 200 ºC for 24 h, after which the mixtures were cooled to room temperature over 500 min. Thereafter, in the processes of ultrasonicing and centrifuging, the obtained MoS$_2$ suspension was washed several times with absolute ethanol and deionized water to eliminate redundant ions, respectively. The dark flowerlike powders were obtained after dried overnight in vacuum at 80 ºC; secondly, the MoS$_2$ precursor was calcined at 400 ºC, 500 ºC, 600 ºC, 700 ºC, 800 ºC and 900 ºC for 2 h, respectively. All heating rates were set at 1 ºC/min. For convenience, the name of the above samples was defined as MoO$_3$-400, MoO$_3$-500, MoO$_3$-600, MoO$_3$-700, MoO$_3$-800, and MoO$_3$-900 according to the calcination temperature, respectively.
On the other hand, the obtained products (MoO$_3$-400, MoO$_3$-500, MoO$_3$-600, MoO$_3$-700, MoO$_3$-800, and MoO$_3$-900) were grinded thoroughly in an agate mortar to form a gas-sensing paste, respectively. Then, the paste was uniformly coated on the alumina ceramic tube in turn, and annealed in air at 120 ºC for 2 h. Here, the gas response magnitude of the sensor is defined as $S = \frac{R_a}{R_g}$, where $R_a$ and $R_g$ are the resistance in air and in the detected gas, respectively. Additionally, the response time and the recovery time were expected to be the minimum time required for the gas sensor output to reach 90% of its saturation after the gas was applied or shut off from the chamber.

2.3 Characterizations

The morphology of the products was investigated by a field emission scanning electron microscope (FESEM, Zeiss Gemini 500). The microstructure of the samples was investigated using X-ray diffraction (XRD, Rigaku Smartlab). X-ray photoelectron spectroscopy (XPS, Termo Scientific Escalab 250xi) was measured to further confirm the surface element composition and chemical state. And the Gas sensing properties were measured by the gas sensing system of MA1.0 (Narui Electronics Co. Ltd., China).

3. Result And Discussion

Figure 1 shows the typical FESEM images of the as-prepared MoO$_3$ samples. Specifically, hierarchical flower-like samples were observed by high resolution SEM images of Fig. 1a-c, which are the samples of MoO$_3$-400, MoO$_3$-500, and MoO$_3$-600, respectively. As a whole, the profile of the three samples are almost same, the microspheres, which the average diameter is less than 1 µm, are constructed by numerous plate-like nanosheets, and the edge thicknesses are about 19 nm. These irregular nanospheres are interconnected each other, facilitating electron transport and ethanol diffusion. After annealing, the hierarchical flower-like morphology was vanished. On the contrary, a lot of nanosheets were synthesized with increased thickness. Interestingly, the nanosheet thickness of sample MoO$_3$-600 become larger than that of MoO$_3$-400 and MoO$_3$-500, due to the growth of the MoO$_3$ crystalline grain at high temperature. In addition, it can be clearly observed that the voids enclosed by numerous primary ultrathin nanosheets with clear texture. Concretely, the diameter of nanoflowers derived from MoO$_3$ calcined in 400 ºC is about 0.3 µm, the sample calcined in 500 ºC is about 0.5 µm, the sample calcined in 600 ºC is about 4 µm. Figure 1d-f show the nanostructures of MoO$_3$ annealed between 700 and 900 ºC. Compared with the samples annealed at lower temperature, the MoO$_3$ annealed between 700 and 900 ºC exhibit the morphology of nanosheets, which represent higher crystallization. What’s more, the thickness of nanosheets is rising with the increase of annealing temperature. The thickness of nanosheets derived from the sample annealed at 700 ºC is 0.031 µm, the sample annealed at 800 ºC is 0.145 µm, and the sample annealed at 900 ºC is 1.690 µm. In terms of crystal growth, almost every point on the unpolished surface of a crystal can be filled with atoms to become the point where the crystal grows. The nanoflowers we obtained above, which has rougher surface than nanosheets, each point on the surface can be filled by atoms so as to becoming smooth and flush through supplying energy by calcining in high temperature. Certainly, as for the smooth surfaces, their consistent growth needs to be thermally
activated [32]. Consequently, the samples obtained with 700–900 °C can grow thicker with the annealing temperature increasing due to the more power and thermal provided.

To the best of our knowledge, the crystallinity, electronic structure and phase stability were strongly influenced by the calcination temperature and composition of the metal oxide semiconductor materials, especially the nanocomposites. Figure 2a shows the XRD patterns of MoO$_3$ samples which were calcined at different temperature. Evidently, the diffraction peaks of all the samples are consistent with the orthorhombic MoO$_3$ (JCPDS 05-0508). The intensity peaks at $2\theta = 12.8$, 25.7, and 39.1 corresponding to (020), (110), (040), (021), and (060) planes, respectively. This indicates that the sample grows with intense preferential orientation of (110). No other diffraction peaks are observed, which confirm that MoO$_3$ samples with relatively high crystal purity. Interestingly, the peak intensity increases with the annealing temperature from 400 to 900 °C, which attributes to the good crystalline at high calcined temperature. On the other hand, the intensities of the peaks were gradually increased with the increase of annealing temperature. It indicates that the crystallinity of the samples was significantly improved via increasing annealing temperature. For example, the intensity of the peak (040) of MoO$_3$-900 is more than three times as compared with that of MoO$_3$-400.

On the basis of the above analysis, the chemical ingredient and the valence state of the elements in the MoO$_3$-600 nanosheets were analyzed via XPS. The corresponding results are shown in Fig. 2b and c. The Mo spectrum in Fig. 2b displays two ?? peaks located at 232.7 and 235.8 eV, ascribe to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, respectively, indicating that the chemical state of Mo element is present as Mo$^{6+}$ in MoO$_3$-600. Further, the energy separation of two peaks is 3.2 eV, which indicates the successful fabrication of MoO$_3$ [30]. The peak of O 1s can be deconvoluted into two independent oxygen species at 529.8 and 531.4 eV (Fig. 2c). The peak at 529.8 eV in the O 1s curve can be attributed to the oxygen ions in the crystal lattice that is lattice oxygen O$_\text{lattice}$ (O$^{2-}$) and surface adsorbed oxygen O$_\text{ads}$. (e.g., O$^-$) [33]. While the other peak at 531.4 eV were assigned to the oxygen ions species such as O$^-$, O$^{2-}$, and O$_2^-$). Compared to the lattice oxygen, the absorbed O$_x^-$ are active to ethanol, so they play a key role in enhancing the sensing performance [34, 35].

In order to investigate the optimum working temperature of different MoO$_3$ samples annealed at various temperature from 50 to 350 °C to 10 ppm of ethanol, as shown in Fig. 3. Evidently, all the sensor's response increase firstly before 200 °C, and then decrease drastically with the increase of operation temperature further. Among them, the MoO$_3$-600 sensor exhibits the maximum response of 8.06 towards 100 ppm ethanol at 200 °C, which is three times higher than those of MoO$_3$-400 and MoO$_3$-900, respectively. Compared with the MoO$_3$-600, the response values of MoO$_3$-400, MoO$_3$-500, MoO$_3$-700, MoO$_3$-800 and MoO$_3$-900 are 3.18, 5.34, 5.81 and 4.50 at 200 °C, respectively. All in all, among all the sensors, the response of MoO$_3$-600 based sensor increases faster than that of others devices such as MoO$_3$-400, MoO$_3$-500, MoO$_3$-700, MoO$_3$-800 and MoO$_3$-900. These demonstrate that the nanostructure and annealing temperature of MoO$_3$ have a considerable effect on the device's response, and inclination
of response increases significantly and then gradually decreases. A suitable working temperature is indispensable in that ample thermal energy is a necessary prerequisite to overcome the chemical barrier of gas and the activation barrier of surface reaction. Besides, when the working temperature is further increased, the gas desorption rate is higher than adsorption rate, which is unfavorable to the response.

Figure 4a gives the dynamic response and recovery characteristics of the MoO$_3$-600 based sensor to different alcohol concentrations from 5 to 500 ppm CH$_3$CH$_2$OH at 200 ºC. Obviously, as the ethanol concentration increases, the response of the MoO$_3$-600 sensor climbs continually, thereafter, the response approaches the saturation value when the CH$_3$CH$_2$OH concentration overpass 500 ppm, see Fig. 4b. The similar results have been reported by other literature [35, 36]. It can be explained that more ethanol molecules can be physically or chemically adsorbed on the MoO$_3$-600 nanosheets, and speeding up the surface reaction rate with the chemisorbed oxygen species such as O$^-$ and O$_2^-$ [30, 36]. Additionally, according to the sensing mechanism of MoO$_3$, the increase of crystallization has an irreplaceable influence on its sensing properties [30, 36]. On the other hand, the limit of detection (LoD) of ethanol was evaluated by the method of linear extrapolation, specifically, the response sensitivity is a function of ethanol concentration (the inset of Fig. 4b). The detailed calculating formula of the LoD is: LoD = 3 × (Standard Deviation/Slope), from which the ultra-low ethanol detection concentration is 125 ppb for the MoO$_3$ sensor. Figure 4c shows a typical repeatability performance of the MoO$_3$ based sensor toward 100 ppm ethanol at 200 ºC, which exhibits its superb stability and repeatability. Moreover, the response time ($\tau_{\text{res}}$) and recovery time ($\tau_{\text{recov}}$) are examined and the results indicate that the MoO$_3$-600 sensor exhibits a very quick response and recovery properties to ethanol (Fig. 4d). Figure 4d gives the $\tau_{\text{res}}$ and $\tau_{\text{recov}}$ of the MoO$_3$-600 sensor toward 100 ppm ethanol, which are 7 s and 26 s, respectively.

From the aspect of practical applications, selectivity is another very important characteristics of the gas sensor. Herein, the sensing properties of MoO$_3$ nanosheets sensor to other various VOCs, for example, benzene, isopropanol, chloroform, acetic acid, methanol and acetone were evaluated. The selective property of the MoO$_3$-600 sensor towards 100 ppm of the above gas at 200 ºC is shown in Fig. 5a. Clearly, the maximum gas response value of MoO$_3$ toward 100 ppm alcohol is 8.06, which is evidently larger than those of other gases. Specifically, the responses to benzene, isopropanol, chloroform, acetic acid, methanol and acetone are 0.23, 1.47, 1.47, 1.57, 1.74 and 2.31, respectively. Therefore, the sensitivity of the MoO$_3$-600 towards ethanol is much higher than that of other VOCs, indicating that it has an excellent selectivity to ethanol.

The sensing mechanism of the MoO$_3$-600 to ethanol can be illustrated by surface conduction modulation model. According to the literature [16, 22], the adsorption and desorption of target gas molecules from the surface of the MoO$_3$-600 could regulate the electrical resistance of gas sensor. When the MoO$_3$-600 is exposed to fresh air, the oxygen molecules (O$_2$) will capture conductive band electrons ($e^{-1}$) to form chemisorbed oxygen ions species (O$^-$ and O$_2^-$). This process will form a depletion layer on its surface region of sensing material, which causes the device resistance increase. When the MoO$_3$-600 sensor was
exposed to ethanol gas, the ethanol molecules can react with the oxygen species \( O^- \) and \( O_2^- \), resulting in the release of trapped electrons back to the conduction band, thereby significantly reducing the sensor resistance. This reaction processes can be expressed as Equations (1) and (2) [37, 38]:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH}_{(\text{gas})} + 6\text{O}_2^{-}_{(\text{ads})} & \rightarrow 2\text{CO}_2_{(\text{gas})} + 3\text{H}_2\text{O}_{(\text{gas})} + 12e^- \quad (1) \\
\text{CH}_3\text{CH}_2\text{OH}_{(\text{gas})} + 6\text{O}^-_{(\text{ads})} & \rightarrow 2\text{CO}_2_{(\text{gas})} + 3\text{H}_2\text{O}_{(\text{gas})} + 6e^- \quad (2)
\end{align*}
\]

4. Conclusion

In conclusion, various \( \text{MoO}_3 \) nanomaterials were successfully prepared by hydrothermal and calcined processes. The nanostructure morphology and crystal quality of \( \text{MoO}_3 \) have temperature-depend relationships. According to the results, the \( \text{MoO}_3 \) morphology can be manipulated by annealing temperature from nanoflowers, nanosheets to nanorods. In addition, the ethanol sensing performances were carefully investigated by \( \text{MoO}_3 \) samples. It is found that the \( \text{MoO}_3 \)-600 has an excellent sensing performance due to the combination of degree of crystallinity and nanostructure.

Declarations

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Conflict of interest

The authors declare that they have no competing financial interest.

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