Study on High-Temperature Synthesis Ejecting Technique of ZnO Nanomaterials

Xiangjun Tang, Junshou Li, Fang Zhao, Kai Han, Bin Song
Army Engineering University, Shijiazhuang, 050003, China

Corresponding author’s e-mail: 18531107787@163.com

Abstract. ZnO nanomaterials were prepared by self-propagating high-temperature synthesis ejecting technique with Al, Cu₂O, ZnO and SnO power reagents as raw materials. The structure and morphology were characterized by XRD, SEM and FTIR methods. The synthesis mechanism of ZnO nanomaterials was discussed. The results showed that single ZnO with hexagonal wurtzite structure was prepared by high-temperature combustion synthesis ejecting method. The products exhibited nanowire morphology, accompanied by granular and flaky morphologies. According to the analysis, the formation mechanism of ZnO nanomaterials is as follows: The reactant is heated to the molten liquid state by exothermic reaction of thermite powder, a self-ejecting system consisting of porous film with high melting point and low density, molten substances to be prepared and ejecting additives is formed by utilizing the difference of specific gravity and melting point between compounds. The substances to be prepared are ejected through the holes of the porous film by the gas released from the ejecting additives, and finally nanomaterials are obtained.

1. Introduction

Nano-zinc oxide (ZnO) is a new kind of multifunctional inorganic material. Because of the grain refinement, the surface electronic structure and crystal structure change, resulting in the surface effect, volume effect, quantum size effect and macroscopic tunneling effect, as well as high transparency and high dispersion which are not available in macro-objects. In recent years, it has been found that it has many special functions in catalysis, optics, magnetism, mechanics and so on, which makes it have important application value in many fields such as ceramics, chemical industry, electronics, optics, biology, medicine and so on. It has particularities and uses that ordinary ZnO can’t compare with. Nano ZnO can be used as ultraviolet shielding material, antibacterial agent, fluorescence material and photocatalytic material in textile, coating and other fields. Because of the series of excellent properties and attractive application prospects, the research and development of nano ZnO has become the focus of many scientific and technical personnel. There are many preparation methods for ZnO nanomaterials, including chemical vapor deposition method, electrochemical method, sol-gel method, solution method, magnetron sputtering method, etc. [1-11]. However, it has not been reported that ZnO nanomaterials are prepared by combustion synthesis ejecting technique.

In this paper, ZnO nanomaterials were obtained by high-temperature combustion synthesis ejecting technique in a self-made combustion synthesis device using Al, Cu₂O, ZnO, SnO powers as raw materials. On the basis of XRD, SEM and FTIR characterization, the reaction mechanism was studied.
2. Experiment

Al, analytical purity, Tianjin Damao Chemical Reagent Factory, ZnO, analytical purity, Tianjin Damao Chemical Reagent Factory, Cu₂O, analytical purity, Shanghai Zhenxin Reagent Factory, SnO, analytical purity, China Pharmaceutical Group Chemical Reagents Co., Ltd. The four reagents mentioned above are used as raw materials, of which Al was the combustion agent, ZnO was the zinc source agent, Cu₂O and SnO were ejecting additives, and the specific formula is shown in Table 1. Experiments were carried out with a self-made combustion synthesis device.

| ZnO:Al:Cu₂O:SnO (Mole ratio) | Reactant weight (g) | Total weight |
|-----------------------------|--------------------|-------------|
| ZnO     Al   Cu₂O   SnO   | 33.2   11.6  30.7  2.9   | 78.4        |

The basic process of the experiment is as follows: Al, Cu₂O, ZnO and SnO powders were dried at 100°C for 2 hours, sifted with 100 meshes of sieve, proportioned in a certain molar ratio, mixed evenly in the mixer for 2 hours, then quickly poured into the reactor of the self-made combustion synthesis device, ignited by tungsten wire, triggered the self-propagating high-temperature synthesis reaction and ejection reaction, the reaction ended within 10 seconds. After natural cooling, a large amount of ZnO nanoparticle powders could be collected in reactor, synthesis furnace wall, breathable cover and pick-up tray. The experiment equipment and process are shown in Figure 1 and Figure 2, respectively.

3. Results and discussion

3.1. XRD analysis

Figure 3 shows the XRD pattern of the product. Compared with the standard ZnO diffraction pattern, each diffraction peak of the product can be indexed without any other miscellaneous peaks, which indicates that ZnO with single wurtzite structure can be prepared by the self-propagating high-temperature synthesis method. The shapes of each diffraction peak of the sample are sharp, which indicates that the degree of crystallization is relatively high.

3.2. FTIR analysis

In order to further study the structure of the products prepared by high-temperature synthetic ejecting method, FTIR characterization was carried out, as shown in Figure 4. FTIR analysis shows that the
absorption peak of the sample near 424-431 cm\(^{-1}\) is formed by the Zn-O bond\cite{12-15}, and the broadening factors can be attributed to the small size effect and the quantum size effect\cite{16-17}. The absorption peaks near 3432 cm\(^{-1}\) and 690 cm\(^{-1}\) are the stretching vibration of O-H bond and the deformation vibration of O-H bond, which are mainly related to the adsorption of water in air. Metal oxides, especially small-sized nanoparticles, have high adsorption activity on the surface. Water will be absorbed on the surface at room temperature in the atmosphere. In most cases, water will eventually dissociate to form adsorbed hydroxyl groups. The absorption peak at 2360 cm\(^{-1}\) is the characteristic peak of CO\(_2\), which can be attributed to the stretching vibration of C-O bond adsorbed on the sample surface. In addition to the above peaks, there are almost no other absorption peaks in the spectra, which further show that the product is a single hexagonal wurtzite ZnO, which is consistent with the phase results characterized by XRD.

![Graph showing X-ray diffraction pattern of the sample.](image1)

**Figure 3.** X-ray diffraction pattern of the sample.

![Graph showing infrared spectra of the sample.](image2)

**Figure 4.** Infrared spectra of the sample.
3.3. SEM analysis
Figure 5 shows the SEM morphology of the product. It can be seen from Figure 5(a) that ZnO has linear structure, uniform radial size and irregular length distribution. Figure 5(b) shows the SEM morphology diagram with local magnification of 50000 times. It can be observed that the surface of ZnO nanowires is smooth and the diameter is within the range of 20~150nm, most of which are within 40~60nm.

In addition to the presence of products in the form of nanowires, occasional agglomeration of nanoparticles is observed, and most single ZnO nanoparticles are approximately spherical in diameter of 30-300nm, most of which are 100-200nm, as shown in Figure 5(c). In some regions, linear, granular and flaky structures coexist in the products, as shown in Figure 5(d).

![SEM images](image)

**Figure 5.** SEM images of the sample.

3.4. Reaction mechanism
Figure 6 is a schematic diagram of product combustion synthesis ejecting principle. In Al + Cu₂O + ZnO + SnO reaction system, the formation of ZnO nanoparticles is accompanied by the self-propagating high-temperature synthesis reaction, and sufficient reaction heat is the necessary condition to maintain the continuous progress of the reaction. The main energy guarantees for the system are three aluminum thermal reactions, as shown in Table 2. The order of heat emitted by the formation of 1mole of Al₂O₃ is aluminum thermal reaction of Cu₂O, aluminum thermal reaction of SnO, aluminum thermal reaction of ZnO.
The combustion synthesis reaction of thermite emitted a lot of heat. The combustion wave propagated from top to bottom, and the system temperature rose rapidly. When the system temperature reached 473K, SnO also had the following reactions:

\[ 2\text{SnO} = \text{SnO}_2 + \text{Sn} \]  

With the further rose of the system temperature, ZnO, SnO2 and Cu2O melted, and the whole system was rapidly in a melted liquid state. The heat transfer process was accompanied by mass transfer process, Al2O3 produced by aluminum thermal reaction was always located at the top of the reaction pool because of its low density, Cu produced by aluminum thermal reaction sank rapidly because of its maximum density, and eventually distributed in the bottom of the reaction pool, above which were Sn and Zn in turn. ZnO, Cu2O and SnO2 after liquefaction distributed in the middle layer because of their similar density and between Al2O3 and Sn, Zn, Cu. As a result, a reaction pool with top-down distribution of Al2O3, ZnO+ Cu2O+SnO2, Zn +Sn +Cu layers was formed. After the combustion reaction, the temperature began to drop, when the temperature dropped to 2327K (Al2O3 melting point), Al2O3 began to crystallize. At the same time, SnO2 in the system continued to gasify (SnO2 boiling point: 2073K), Cu2O continued to decompose the metal Cu and O2 (Cu2O decomposition temperature: 2073K), i.e. reaction (2), resulting in many permeable holes in Al2O3 ceramic layer. Zn substituted by the aluminum thermal reaction of ZnO combined with O2 decomposed from reaction (2) to form ZnO, i.e. reaction (3), which was ejected from the above-mentioned holes under the pressure of internal gas, and finally formed ZnO nanowires.

\[ 2\text{Cu}_2\text{O} = 4\text{Cu} + \text{O}_2 \]  

\[ 2\text{Zn} + \text{O}_2 = 2\text{ZnO} \]  

As shown in Figure 5 at A, B and C, it can be seen that nanowires have slightly thicker "thread heads", which are directly related to the gasification and injection process in the reaction process. With the
release of \( O_2 \) and gasification of \( SnO_2 \) in the middle layer, the pressure in the chamber increased continuously, which caused \( ZnO \) to break through the blockade of \( Al_2O_3 \) melt and ejected from \( Al_2O_3 \) holes. Because the temperature at the outlet of \( Al_2O_3 \) hole was higher than that of the external environment and lower than that inside the chamber, \( ZnO \) ejected from the chamber to the outside of the chamber and underwent the process of condensation and solidification. \( O_2 \) release and \( SnO_2 \) gasification resulted in pressure drop in \( Al_2O_3 \) ceramic chamber, and the release rate of \( ZnO \) decreased accordingly. At the outlet of \( Al_2O_3 \) ceramic hole, it condensed into a mushroom-like molten drop, and tended to solidify with the decrease of temperature, thus playing a temporary sealing role. As the reaction continues, the pressure in the cavity of \( Al_2O_3 \) ceramics cavity began to increase. When the pressure increased to a certain extent, the newly condensed \( ZnO \) was forced to eject from the cavity of \( Al_2O_3 \) ceramics. As a result, the mushroom-like droplets solidify into thick "thread tails". The above process was repeated until the end of the reaction. With the ejection of \( ZnO \) nanowires, the pressure in the \( Al_2O_3 \) ceramics cavity decreased rapidly, so the flying speed of the “head” of \( ZnO \) nanowires was much higher than that of the “tail”. This difference of velocity led to the dynamic stretching process of the \( ZnO \) nanowires in flight, and finally formed the \( ZnO \) nanowires with mushroom-like heads. When the velocity difference between the head and the tail was large, the \( ZnO \) nanoparticles could be obtained by separating them during the stretching process. Some nanoparticles continued to grow around and became flaky structures under the continuous action of energy.

4. Conclusions

\( ZnO \) nanomaterials with single wurtzite structure were prepared by high-temperature combustion synthesis ejecting technique with \( Al, Cu_2O, ZnO \) and \( SnO \) power reagents as raw materials. The morphology of the product is mainly linear, accompanied by granular and flaky. The product synthesis mechanism is as follows: three aluminum thermal reactions provide energy guarantee for the self-propagating high-temperature synthesis reaction, the \( O_2 \) produced by high temperature decomposition of \( Cu_2O \) and the high temperature gasification of \( SnO_2 \) are the main reasons for nano-\( ZnO \) ejecting. After three processes of combustion synthesis, gasification ejecting and dynamic stretching, linear \( ZnO \) nanomaterials were obtained. When the \( ZnO \) nanowires were stretched apart, the granular and flaky structures can be obtained.

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