Morphology Study by Using Scanning Electron Microscopy

Fei Liu, Junshu Wu, Kunfeng Chen and Dongfeng Xue*

State Key Laboratory of Fine Chemicals, Department of Materials Science and Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, P. R. China

*Corresponding author. Email: dfxue@dlut.edu.cn

The synthesis and characterization of micro- and nanomaterials have received broad attention and become a leading edge in materials science and technology. Functional micro- and nanomaterials endow us the possibility to develop devices with distinguished performance in electronics, magnetics, optics, and photonics. In addition to the composition, the size and shape are two other important factors that determine properties of functional materials. One of the major challenges in this active field is the study of morphology-controlled crystal growth process. The structure of crystalline solid, whatever is its dimension, can be characterized by several means such as X-ray diffraction and microscopy, for micro- and nanomaterials, use of electron microscopy is necessary. In this chapter, we will present how microstructures of some important functional materials are characterized by employing scanning electron microscope (SEM). The sample fabrication technique for these special materials (crystalline powders and nanostructured films) will also be discussed. We will cite, for example, microstructures of Cu-base, Zn-base and Nb-base compounds. Structure evolutions and formation mechanisms are discussed based on the observation from SEM. These results indicate that SEM is a very powerful tool to study the crystal growth morphology and assist the micro and nano-fabrication.

Keywords Scanning electron microscope, morphology, micro- and nanomaterials, fabrication, structure evolution

1. Introduction

Materials made with unique sizes and structures are expected to find various novel applications. The discovery of novel materials, processes, and phenomena at the micro- and nanoscale, as well as the development of new experimental and theoretical techniques for research provide fresh opportunities for the development of innovative nanosystems and nanostructured materials, which is likely to have a profound impact in areas such as electronics, medicine, energy, and biotechnology [1–4]. Development of nanomaterials requires advanced tools and skills to survey in high magnifications, understand nanostructures, and improve fabrication strategies. Light cannot be used to see the nanoworld, as its resolution is limited by its own wavelength, so optical microscopes are useless for nanotechnology. Electron microscopes use electrons instead of photons, because electrons have a much shorter wavelength than photons and so allow observing matter with atomic resolution. Generally, there are two types of electron microscopes, transmission electron microscope (TEM) and scanning electron microscope (SEM). TEM shoots electrons through the sample and measures how the electron beam changes as it is scattered in the sample; SEM images the sample surface by scanning it with electron beams in a raster scan pattern. The electrons interact with the sample atoms producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. Because the electrons in a TEM pass through the sample, it is commonly used to look at the internal structure of the sample, while SEM looks at the surface (or the near-surface) [5].

Signals produced by an SEM result from interactions of the electron beam with atoms at or near the surface of the sample, include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons [5]. By detection of secondary electron, SEM can produce vivid images of a sample surface (secondary electron image, or SEI), with superior resolution about 1 to 5 nm. Due to the relative narrower electron beam, SEM has a much greater depth of field (that is, the depth over which the object remains in focus) than TEM, thus yielding a characteristic three-dimensional appearance useful for investigating the surface of objects which have a complicated topography. Characteristic X-rays are emitted as the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These X-rays can be used to identify and quantitively determinate the elements in samples. BSE are produced by elastic interactions of beam electrons with nuclei of atoms in the specimen. Since heavy atoms with a high atomic number are stronger scatterers than light ones, images with BSE contain compositional information and the distribution of different elements in the sample can be get from BSE images.

In this review, we will demonstrate how SEM is used to investigate the crystal growth or structure evolution processes in our work. Solution-based strategies were employed in these cases because they can enable great chemical flexibility and synthetic tunability and many unique inorganic materials can be synthesized by these approaches. Based on the SEM observation of samples obtained at different fabrication parameters, some reasonable mechanisms were proposed to explain the structure evolution process. Energy diffraction X-ray spectrum (EDX) which is integrated in SEM system and X-ray diffraction spectrum (XRD) are also used to identify the composition and crystal phase of the samples. These cases indicate that SEM is a very powerful tool to study the crystal growth morphology and assist the micro- and nanofabrication.
2. SEM observation of Cu₂O structure evolution

Cuprous oxide (Cu₂O) is a p-type semiconductor with a direct band gap of 2.17 eV and a large exciton binding energy of 140 meV, which has many potential applications in catalysis, gas sensors and optical limiters [6,7]. As a face-centered cubic (fcc) transition metal oxide, the Cu₂O crystal crystallizes in cuprite structure, space group Pn-3m [8,9]. The preferable morphology of Cu₂O single crystal is polyhedron (such as cube, cuboctahedron or octahedron), according to Wulff facets theorem, defined as a crystal has to be bounded by facets giving a minimum total surface energy at equilibrium [10]. In the past decade, many studies have reported diverse shapes of Cu₂O micro- and nanocrystals, such as cube, octahedron, cuboctahedron, rhombic dodecahedron and branching shape [11]. Although great progress has been made in the general synthesis of Cu₂O micro- and nanostructures by subtly changing the experiment parameters, size and morphological control for Cu₂O still remains as a challenging subject of research. The Cu₂O micro- and nanocrystals can be good examples for SEM teaching, owing to their abundant morphologies.

Most of the Cu₂O micro- and nanocrystal preparation methods are based on the reduction of Cu(II) ions. When alkali present in solution, the reaction takes place according to the follow equation

\[
2Cu^{2+} + R + 2OH^- \rightarrow Cu_2O(s) + H_2O + R^{2+} \quad (R \text{ denote reductants})
\]

When the reaction occurs in acid or neuter environment,

\[
2Cu^{2+} + R + H_2O \rightarrow Cu_2O(s) + 2H^+ + R^{2+}.
\]

2.1 Branching shape evolution

Branching crystal growth patterns have fascinated scientists for several centuries. Branching growth occurs as a by-product of the competition between three distinct physical phenomena: diffusion, capillary forces (due to surface energy effects) and crystalline anisotropy [12]. In recent years, various Cu₂O branching growth patterns have been synthesized with different methods and strategies [8,13,14]. In our group, 64 kinds of Cu₂O branching patterns have been successfully synthesized by using EDTA as reductant and chelating ligand [8]. The obtained branching shapes of Cu₂O microcrystals are based on five branching growth patterns which almost cover the full range of branching growth of cubic crystal system.

As shown in Fig. 1, the 6-pod, 8-pod, 12-pod and 24-pod branching shapes have symmetrical branching growth direction. The growth direction of 6-pod branching structure is six <100> directions, as for 8-pod branching shape is eight <111> directions, 12-pod branching growth pattern is twelve <110> directions. The novel 24-pod branching shape is more sophisticated. Each pod of 8-pod branching structure divides into three pods and thus forms the 24-pod branching shape. Therefore 24-pod branching shape could derive from the other two branching structure, 6-pod and 12-pod branching shapes. In this condition, the selective adsorption of EDTA molecules on different crystallographic planes is a key parameter to determine the different branching growth morphologies. The molar ratio of EDTA/Cu(II) and pH of the initial solution can be adjusted delicately, thus the relative growth rate of {100} and {111} facets of Cu₂O can be well controlled.

The EDTA molecules play multiple roles in the present approach. Firstly, a divalent copper complex with EDTA ligands was prepared as copper precursor. Then EDTA reduces Cu(II) to Cu(I), subsequently, more EDTA can also
chelate with Cu(I) to form Cu(I)-EDTA complex. Finally, the EDTA molecules adsorb on different surfaces of as formed Cu₂O crystal, which prevents Cu(I) from bonding to the surface oxygen atoms [9].

2.2 From cube and octahedron to multipod shape

Cu₂O microcrystals with different morphologies can also be synthesized by the reaction of glucose and different copper salts under alkaline conditions without introducing any template or surfactant. Our recent studies show that Cu₂O branching growth habit is closely related to the pH value [8,9,13,14]. In order to prove the versatile effect of pH value on morphology evolution, different copper sources have been introduced to this system.

A series of morphology evolutions of Cu₂O microcrystals, from octahedron or cube to multipod branching shapes has been observed by adjusting system pH value with Na₂CO₃. The 6-pod, 8-pod and 24-pod branching shapes have been successfully synthesized by using glucose as reducer in hydrothermal method.

Fig. 2 shows the SEM images of the Cu₂O microcrystals obtained in different reaction conditions. From the overview images, the shape of Cu₂O microcrystals can finely transform from polyhedron to multipod branching shape by manipulating the concentration of Na₂CO₃. In Fig. 2a₁, the shape of Cu₂O products is cube with size of about 2 µm, and some Cu₂O microcrystals are not well-defined, with their vertexes extending outwards from the core. The exposed surfaces of cube are six {100} facets, according to fcc structure of Cu₂O crystal. The eight vertexes extend more with the increase of Na₂CO₃ concentration, leaving the shallow indentions in the centers of surfaces and finally growing into 8-pod branching shape (Fig. 2a₂) which grows along <111> direction.

Similar morphologies can also been obtained by using different copper resources. With CuSO₄ and Cu(CH₃COO)₂ as reactant, the six {100} facets are rough and some corners of the cube disappear (Fig.2b₁). The formation process of 8-pod branching shape is similar as shown in Fig. 2a. However, novel 12-pod and 24-pod branching shapes are presented in this system. The preferential crystal growth along twelve <110> directions results in the formation of 12-pod branching crystals, and the 24-pod branching shape is formed by dividing each pod of 12-pod branching shape into two pods (Fig. 2b₂).

The morphology of Cu₂O microcrystals has a significant change with CuCl₂ as reactant, transforming from octahedron to 6-pod branching shape (Fig. 2c ). The anions play an important role in determining the final shape of Cu₂O microcrystals. The effect of Cl⁻ on morphology is different from the other anions, such as SO₄²⁻, CH₃COO⁻ and NO₃⁻. At low pH value, octahedron with rough surface and some with {110} truncated has been obtained (Fig. 2c₁). The crystal growth along the six vertexes of octahedron (<100> direction) is faster than the center of {111} facets, and then 6-pod branching Cu₂O microcrystals are formed (Fig. 2c₂).

The formation processes of Cu₂O branching nanostructures have been demonstrated on the base of the diffusion-limited branching growth mechanism [8, 9]. In general, the degree of branch increases with the pH increase. When pH increased to a given value, reduction power of glucose enhances, with the fact that the reaction even could take place at room temperature. Both the reduction rate and the growth rate increase with adding more alkali. Therefore the growth rate is faster than the diffusion rate, resulting in the branching growth. With the enhanced reduction power of glucose at high pH value, the high concentration of precursor Cu⁺ ions is formed in a short time and the Cu₂O nuclei also appear in solution spontaneously. At Cu₂O crystal growth stage, crystal growth consumes large amount of Cu⁺ ions, which form a depletion zone of the Cu⁺ ions around the growing crystals. Owing to the higher concentration of Cu⁺ ions in initial solution, the concentration gradient for Cu⁺ ions between the vertexes and center of facets trends to be large. A concentric diffusion field is formed, generating various Cu₂O branching microcrystals.
At low pH value, the growth rate and the concentration gradient for Cu\(^{2+}\) ions is low. At this condition, the Cu\(_2\)O microcrystals preferably grow into the thermodynamically more stable morphologies, such as cube and octahedron. At high pH value, non-equilibrium morphologies (branches) can be stabled. The enhancement of reduction power of glucose further increases the concentration of Cu\(^{2+}\) ions. At the same time, compared with the diffusion rate, the growth rate is large enough to aggravate the concentration gradient and the complicated 24-pod branch pattern is achieved.

### 2.3 Core-shell structure

The syntheses of hollow and porous Cu\(_2\)O micro- and nanostructures have been the subject of many recent investigations due to their high surface area and low material density [7,15]. Several hollow Cu\(_2\)O micro- and nanocrystals with defined interior architectures have been prepared previously through different methods [2,10]. Xue and co-workers have synthesized core-shell Cu\(_2\)O microcrystals by hydrothermal method [10]. In this procedure, ethanol acts as a reducing agent and tartaric acid promotes the formation of monodispersed intermediate microspheres. Subsequently, ethanol reduces this template to Cu\(_2\)O and the core-shell Cu\(_2\)O microspheres are formed by inside-out Ostwald ripening.

As shown in Fig. 3a, the size and morphology of the intermediate microspheres are uniform. The Cu\(_2\)O microspheres are presented in Fig. 3b, after the intermediate microspheres transform into Cu\(_2\)O microcrystals, the size of microspheres become larger and the size distribution is broadened. The surface of microspheres is rougher in contrast to the intermediate microspheres. Some microspheres are broken and the core/shell structures can be observed. Fig. 3c and 3d indicate that the shells of some microspheres collapse into pieces. The bowl-like microsphere has a core inside and the shell wall consists of tightly aggregated nanoparticles with diameters of ca. 200 nm.

![Fig. 3 SEM images of the morphology evolution process of Cu\(_2\)O microcrystals.](image)

**Fig. 3** SEM images of the morphology evolution process of Cu\(_2\)O microcrystals, a) the intermediate microspheres, b) the obtained Cu\(_2\)O microspheres, c) and d) the enlarged SEM images, which show the core-shell structure. Scale bar = 5 µm.

To understand the formation process of the core-shell structured Cu\(_2\)O microspheres, the morphology observation at different time is conducted. At 1.5 h, green precipitate is obtained and the intermediate products are monodisperse microspheres (Fig. 3a), which is promoted by combined effect of tartaric acid molecules and the mixed solvent solution. At 14 h, the core-shell structured Cu\(_2\)O microspheres are obtained and the XRD data prove that the final products are pure Cu\(_2\)O microcrystals (see reference [15]).

Furthermore, the formation mechanism has been proposed based on SEM observations: (i) formation of intermediate microspheres; (ii) reductive conversion of this template to Cu\(_2\)O; (iii) inside-out Ostwald ripening of Cu\(_2\)O microspheres. This method largely depends on the effective formation of intermediate microspheres and Ostwald ripening process in the hydrothermal condition.

### 2.4 Polyhedron structure

Recently, the shape evolution of Cu\(_2\)O from cube to octahedron has been reported by many researchers using different synthesis methods [6]. The systematic and delicate geometry control of Cu\(_2\)O polyhedron has been achieved by taking advantage of the selective surface stabilization effect. The three lowest index planes of Cu\(_2\)O polyhedron is \{100\}, \{111\}, \{110\}, and the polyhedra based on these three planes have all been synthesized. The formation of these polyhedra can be greatly controlled by introducing different additives [6,11].

We have studied the effect of Cl\(^-\) ion and PVP on morphology of Cu\(_2\)O microcrystals by using formic acid as reductant while ethanol and water as solvent. Without adding Cl\(^-\) ions, the well-defined Cu\(_2\)O cube has been obtained. From SEM images (Fig. 4a), the cube with size of about 4–6 µm has perfect surfaces and sharp corners. The \{110\} truncated cube are successfully synthesized by a hydrothermal process with use of Cl\(^-\) ion as a structure direct additive. As shown in Fig. 4b, the exposed surfaces of the \{110\} truncated cube are made of 6 squares of \{100\} facets...
and 12 hexagons of \{110\} facets, which has 48 edges, 32 vertices. In this polyhedron, two types of vertices exist, one is the joint of three hexagons, and the other is the joint of two hexagons and one square. The relative surface energies of Cu_2O crystals are in the order of \(\gamma\{111\} < \gamma\{100\} < \gamma\{110\}\). To minimize the total surface energy, the introduction of Cl^- ions will selectively adsorb onto the higher energy \{110\} surfaces. The adsorption stabilizes the \{110\} facets and thus the growth rate perpendicular to this facet is slower than that of \{100\} facet. This leads to the exposure of \{110\} surfaces and the formation of final \{110\} truncated Cu_2O polyhedra.

The presentation of PVP changes the growth environment of Cu_2O microcrystals which grow into irregular branching shape. When more PVP molecule is introduced, the degree of irregular branch falls, leading to sphere-like shape. In addition, the ratio of ethanol and water and the amount of formic acid also have important influence on the shape of Cu_2O microcrystals.

![Fig. 4 SEM images of Cu_2O microcrystals prepared with different inorganic ions. Formic acid is used as reductant, a) without or b) with the addition of Cl^- ions. In glucose reduction system, c) without additives, d) Cl^- ions, e) Br^- ions, f) F^- ions. Scale bar = 2 \(\mu\)m.](image)

The effect of the inorganic ions (F^-, Cl^-, Br^-) on shape of Cu_2O microcrystals is different in our glucose system. With F^- ions as the additive, the shape of Cu_2O microcrystals is cube (Fig. 4f), which is identical to the product without addition of any additive (Fig. 4c). When introducing Cl^- ions, sharp corners and smooth surfaces are the character of these cubic crystals (Fig. 4d). With the presence of Br^- ions, the truncated cube is obtained with eight small \{111\} facets and six large \{100\} facets (Fig. 4e). Br^- ion will selectively adsorb onto the \{111\} surfaces during the crystal growth and hinder the growth rate perpendicular to it. Therefore, additives can change the order of free energies of different facets and thus influence the growth rate of different facets, leading to formation of different shapes.

### 3. SEM observation of ZnO structure evolution

As a multifunctional semiconducting metal oxide, ZnO exhibits a combination of interesting properties including room-temperature wide band gap (3.37 eV), large exciton binding energy (60 meV), high electron mobility (100 cm^2 V^-1 s^-1), optically transparent electrical conductivity, and piezoelectricity. To date, ZnO has received considerable attention because of its versatile technological applications in photocatalysis, light emitting diodes, nanogenerators, dye-sensitized solar cells and gas sensors, etc. [16–21]. The properties of ZnO are highly dependent upon crystal shapes and surface characteristics, which spur worldwide interest on morphology study of ZnO nanostructures in modern materials science. Wurtzite ZnO has a hexagonal structure with space group \(P6_3\text{mc}\). The crystal structure are expressed with both polar and nonpolar facets. Positively charged Zn-(0001) and negatively charged O-(000\(\bar{1}\)) are perpendicular to the c-axis, and \{10\_0\} is side planes that are parallel to the c-axis. Zn\(^{2+}\) sits inside the tetrahedron constructed by O\(^{2-}\), and these tetrahedrons interconnect one another through corner sharing. The structure can be simply described as a number of alternating planes composed of tetrahedrally coordinated O and Zn, stacked alternately along the c-axis. Owing to its wurtzite structure and polar crystal surfaces, ZnO exhibits a diverse group of growth morphologies for particles and thin films. Morphology study still remains the ultimate goal in the discovery of novel micro- and nanoscale properties and is essential for the success of “bottom-up” approaches toward future devices. The objective of this section is to review the unique ZnO micro- and nanostructures obtained in our group and their corresponding growth mechanism revealed with SEM.

#### 3.1 Solid-liquid interface reaction to the growth of ZnO thin film

A method of engineering nanorod and nanotube arrays on zinc metal substrates by solid-liquid interface reaction has been developed, which combines the growth of 1D microstructure with their self-assembly into ordered thin films [22]. The \textit{in situ} solution chemistry modifies Zn metal substrates by surface-corrosion strategy, and there are no use of templates, surfactants and catalysts in this process. Therefore, various surface structures can be facilely fabricated on interface regions with a thickness of micrometers by controlling the oxidized dynamic process across the interfaces.
Zinc foil is a conductive material, making it easy to utilize the well-aligned ZnO nanorod thin film for electronic and optoelectronic devices. As a typical sample, we have synthesized vertically aligned ZnO nanorods with uniform diameter and length on a Zn foil using ammonium persulfate as oxidant. The reactions that accounts for the ZnO nanorod growth are essentially a surface oxidation process:

\[(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{HSO}_4 + \text{H}_2\text{O}_2\]  \hspace{1cm} (3)
\[\text{Zn} + \text{H}_2\text{O}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}\]  \hspace{1cm} (4)
\[\text{ZnO} + 4\text{KOH} \rightarrow \text{Zn(OH)}_4^{2-} + 4\text{K}^+\]  \hspace{1cm} (5)

In this solution system, a dissolution-recrystallization mechanism is responsible for the growth of ZnO nanorods. Initially, the hydrothermal oxidation induces a large quantity of ZnO nucleation layers, reducing the interface energy barrier for ZnO growth (reaction 3 and 4). However, the fresh seed film can be dissolved in KOH solution, \(\text{Zn(OH)}_4^{2-}\) growth units are successively supplied with the oxidation and dissolution of metal, resulting in the epitaxial growth of nuclei into 1D ZnO microstructures. Images of the surface structures are gained using SEM, as shown in Fig. 5a. The top view shows that ZnO nanorods cover the Zn substrate uniformly, indicating that ZnO nanorods are indeed grown from the Zn metal instead of a random deposition of ZnO particles on the surface. These rods have a diameter of about 200 nm and length up to micrometers.

According to the solubility difference between ZnO and ZnS, a thioglycolic acid-assisted surface modification route can be used to convert these ZnO nanorods into ZnS nanotubes. \(\text{HSCH}_2\text{COOH}\) increases the activity of \(\text{Zn}^{2+}\) on ZnO nanorod by coordination reaction, which enables ZnS to nucleate and crystallize by consuming ZnO templates. The time-dependent observation using SEM is displayed in Fig. 5, revealing the variation of Zn surface from nanorod to nanocable and finally nanotube. The whole Zn surface modification strategy provides a promising technique for fabricating oxides and sulfides on other metals.

The transition metal Zn is usually used to constitute primary cell (e.g., Daniell cell) to convert chemical energy into electrical energy. Each cell consists of two half cells, where an oxidation half-reaction or a reduction half-reaction takes place respectively. The more active metal Zn is anode and the less active metal (e.g., Cu) is cathode. Based on a modified galvanic replacement reaction, an electroless deposition method in an acidic medium is developed to synthesize ZnO taper-tube film on Zn substrate [23]. The electroless deposition process is conducted in \(\text{CuCl}_2\) solution, where acetic acid is added to tune the pH value and \(\text{H}_2\text{O}_2\) is used to produce \(\text{O}_2\). Zn metal atom from Zn electrode loses electrons and enters the solution as the Zn\(^{2+}\) ion. The half-equation is:

\[\text{Zn(s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e} \]  \hspace{1cm} (6)

In the forward process, \(\text{Cu}^{2+}\) and \(\text{O}_2\) in solution consume electrons, which results in Cu deposition and OH formation. Cu nanoclusters and vicinal Zn domains act as local cathodes and anodes of micrometer-sized cells on Zn foil, realizing a modified galvanic replacement reaction. OH\(^-\) migrates and reacts with Zn\(^{2+}\) in anode regions, generating ZnO crystals.

Polar oxygen planes and top tetrahedron corner-exposed polar zinc faces are metastable in ZnO crystal, and low-index faces consisting of nonpolar \{10\_0\} planes are stable. Accordingly, metastability of the polar surface can be utilized to create tubular structures by minimizing or eliminating \(\{00\_1\}\) planes. SEM inspection suggests the growth of ZnO taper-tube is a selective etching process. As shown in Fig. 6a, \(\text{ZnO}\) truncated tapers are firstly formed on Zn substrate between migrated \(\text{OH}^-\) from cathode and resultant \(\text{Zn}^{2+}\) in anode regions. The etching on the top \(\{00\_1\}\) planes initiates at six corners owing to their high surface energy. The pH value is a key parameter to determine the thermodynamic stability of active sites, which is adjusted to 2.6 through the addition of acetic acid. These six holes are widened with reaction time and continue to serve as active sites for subsequent etching until complete removal of ZnO core (Fig. 6b). The whole process is shown in Fig. 6a: \(\text{d}_1\) \(\rightarrow\) \(\text{d}_1\). Such a growth pattern also allows an expansion along the radial direction while maintaining 1D configuration.

![Fig. 5 Morphology evolution from ZnO nanorod to ZnS nanotube. Scale bar = 1 \(\mu\text{m}\).](image-url)
The growth mechanism of oxidation products is understood by simply inspecting morphologic variation with SEM. This facile methodology provides a clear perspective for electroless deposition route, which is important to prepare other oxides through selecting appropriate electroless galvanic reactions.

By changing the supersaturation of Zn-containing precursors, the growth pattern and the morphology of resultant particles from homogeneous growth can also be controlled in solid-liquid interface reactions [24]. In Zn-formamide-ethanol ternary system, when ZnAc₂ aqueous solution is used to increase the concentration of [Zn(formamide)₆]^{2+}, white deposition is found on the surface of the Zn substrate as well as in the solution. SEM observation indicates that the alcohol thermal process generates hexagonal ZnO architectures via selective chemical etching. The etching process is related to ZnO crystallographic characteristics of surface polarity and chemical activities. Fig. 6a−e₂ shows SEM images of ZnO nanoparticles at different reaction time. One can see that chemical etching leads to an obvious boundary on the side surface which divides the well-crystalline hexagonal microcrystal into two parts (Fig. 6c). Then a hole at the middle emerges, which further extended through the thickness of the microdisk. Finally, faceted hexagonal microrings are formed (Fig. 6d).

3.2 Ion exchange reaction for the synthesis of ZnO

Ion exchange provides a facile method for systematically varying the compositions and morphologies. The evolution process can lead to various interesting patterns of segregated domains in precursors, and finally a new micro- and nanostructures. SEM shows superiority in the investigation of morphological reorganization during the ion exchange reaction. The images can directly reflect the effect of critical size and precursor shape, epitaxial relationship between the two phases, and activation energies for diffusion of atoms or ions on creating structures with high structural complexity.

Recently, a novel spontaneous ion exchange route is established on the base of solubility difference to synthesize a number of metal oxides (e.g. ZnO, CuO, Mn₂O₃, CdO, CaO) [25, 26]. This strategy has been extended to prepare ZnO hollow spheres with Zn₅(CO₃)₂(OH)₆ microstructures by anion exchange [27]. In this process, the Zn₅(CO₃)₂(OH)₆ microspheres serve as sacrificial templates on which the ZnO shell grows while the precursor core is consumed simultaneously. Zn₅(CO₃)₂(OH)₆ microspheres can be converted into ZnO filled microspheres by aging reactions. Subsequently, these ZnO microspheres grow at the expense of the metastable ZnO cores by Ostwald ripening. Hollow
ZnO shells can be produced finally by the anion exchange and ripening procedures. Some main chemical process can be described as follow:

\[
\begin{align*}
Zn_6(CO_3)_3(OH)_6 &\leftrightarrow 5Zn^{2+} + 6OH^- + 2CO_3^{2-} \quad (7) \\
Zn^{2+} + 2OH^- &\rightarrow ZnO (s) + H_2O \quad (8) \\
ZnO (s) + 2OH^- &\rightarrow ZnO_2^{2-} + H_2O \quad (9)
\end{align*}
\]

The solubility product constant \( K_{sp} \) for Zn(OH)\(_2\) is lower than that of ZnCO\(_3\), therefore, OH\(^-\) anions with high concentration makes reaction 7 take place, accelerating the formation of ZnO (reaction 8). Interior ZnO particles with smaller sizes eliminate owing to their high surface energy (reaction 9). The formation process of ZnO hollow spheres has also been shown by the SEM images (Fig. 7a, Fig. 7b, Fig. 7b\(_2\)). Hollow ZnO microspheres are prepared by direct treatment of Zn\(_6\)(CO\(_3\))\(_3\)(OH)\(_6\) in alkaline KOH solution. SEM images show that the shell of the ZnO architecture consists of numerous nanoparticles (Fig. 7b\(_2\)).

**Fig. 7** The microscopic conversion from Zn\(_6\)(CO\(_3\))\(_3\)(OH)\(_6\) templates a) to ZnO architectures b\(_1\), b\(_2\) and ZnS c\(_1\),c\(_2\) architectures. Scale bar =10 \( \mu \)m.

With the help of SEM, new crystalline ordering and new phenomena displayed by hollow structures can be well researched. ZnS spherical shells have been prepared via a spontaneous anion exchange reaction between Zn\(_6\)(CO\(_3\))\(_3\)(OH)\(_6\) templates and Na\(_2\)S [28]. The preparation of ZnS shells involved an initial formation of ZnO-ZnS core-shell composites and a subsequent remove of ZnO in KOH solution. As shown in Fig. 7, Zn\(_6\)(CO\(_3\))\(_3\)(OH)\(_6\) microsphere templates have coarse surface (Fig. 7a\(_1\)), which becomes smooth once the replacement reaction takes place in Na\(_2\)S solution (Fig. 7c\(_1\)). By prolonging reaction time, ZnO-ZnS core-shell structures are formed and the spherical shells are gradually separated from their inner cores with the retainment of the surface morphology (Fig. 7c\(_2\)). The as-obtained core-shell structures are further treated in KOH solution, generating the pure ZnS shells (Fig. 7c\(_3\)).

The solubility difference drives the replacement of OH\(^-\) and CO\(_3\)^{2-} dissociated from Zn\(_6\)(CO\(_3\))\(_3\)(OH)\(_6\) by S^{2-} when an appropriate amount of Na\(_2\)S is introduced into the solution. Zn\(_6\)(CO\(_3\))\(_3\)(OH)\(_6\) microspheres can be in situ converted into ZnO spheres in alkaline Na\(_2\)S solution. High surface activity and lower solubility enable ZnS to grow on the surface of ZnO microspheres by consuming out layers. Moreover, if thioacetamide acts as sulfur source instead of Na\(_2\)S, only ZnS nanocrystals are gained. These facts demonstrate that Na\(_2\)S is both alkali and sulfur sources, enabling ZnO and ZnS to grow by different chemical processes. By arresting a series of intermediate morphologies in the anion exchange process by SEM, we make the growth of core-shell and hollow structures clear, which helps to analyze and fabricate other hierarchical composites with unique hollow architectures by employing sacrificial template routes.

**4. SEM observation of crystal structure evolution in Nb-based materials**

Niobium oxide and niobates have emerged as novel materials with enormous technological and scientific interest because of their excellent nonlinear optical, ferroelectric, piezoelectric, electrooptic, pyroelectric, photo refractive and catalytic properties [29]. In the following part, we present the SEM study of structural evolution of several Nb-based materials, the change in crystal morphologies in these cases are caused by solution pH value variation, ligand alteration and more specifically, crystal phase transformation. Such structural evolutions provide a marvelous opportunity for selecting Nb-based materials with desired morphologies and structures through kinetic control of the reaction.
4.1 Structure evolution of Nb$_2$O$_5$ in solution

By simply treating Nb foil in HF aqueous solution under hydrothermal conditions, a thin layer of products composed of Nb$_2$O$_5$ can be obtained [30]. The oxidation process of metal Nb is based on the naturally dissolved oxygen in water, which is an electrochemical process, and due to the present of $F^-$ ions in solution, this spontaneous oxidation reaction can be accelerated drastically due to their strong corrosion ability to Nb metal. It has been found that the nanostructure of this oxide layer was very sensitive to the concentration of HF and pH value of the solution, thus a structure evolution process of the products can be observed. Nanostructures including ribbons, polyhedrons, plates and rods can be obtained via selecting different reaction conditions.

![Fig. 8](image)

**Fig. 8** SEM illustration of Nb$_2$O$_5$ structure evolution caused by system pH change. a) nanobelts, b) twined polyhedron, c) plates, d) wheel-like structure, e-h) nanorods with different branching degrees. Scale bar a-d) 2 µm, e-h) 1 µm.

SEM images of the samples in Fig. 8 illustrate the interesting morphological evolution of Nb$_2$O$_5$ with the decrease of pH value in the reaction system. In the higher pH (10) environment, a large quantity of nanoribbons are formed with width of about 300 nm and length up to several micrometers, these ribbons have high aspect ratio and appeared to be flexible (Fig. 8a). In a lower pH system, it leads to the formation of microcrystals with regular twined polyhedra shape in a large-scale, as shown in Fig. 8b, the edge length of these polyhedra ranges from 2 to 3 µm, it can be clearly found that this structure is constructed by two polyhedra, as a star-shape, each polyhedron is rotated 90° from its counterpart.

Further decreasing pH value of the initial reaction system, Nb$_2$O$_5$ crystallites with plate-like morphology is obtained (Fig. 8c). The edge length of these plates is about 2 µm, interestingly, these plates can self-assemble into wheel-like structures, which are composed of several plates (Fig. 8d). It is well accepted that the crystal morphology are determined by both intrinsic (crystal structure) and extrinsic factors (crystal growth environments). Considering that no additional surfactants or templates are added into the reaction system, the formation of various shapes is supposed to be the different growth habit for Nb$_2$O$_5$ polymorphs. Nb$_2$O$_5$ is found to exist in different crystal phases, H-Nb$_2$O$_5$ (pseudo-hexagonal), O-Nb$_2$O$_5$ (orthorhombic), and M-Nb$_2$O$_5$ (monoclinic), the change in system pH value may alter the stability of different phases in solution, thus Nb$_2$O$_5$ crystallites with desired particle morphology can be obtained.

Furthermore, by carefully changing the system pH value in a precisely controlled range, branched nanowires can be obtained, and the branching degree can be deliberately adjusted. SEM observation of this process is shown in Fig. 8e–h. Nb$_2$O$_5$ grown under pH = 3.7 are nanorods with no branches (Fig. 8e), as the pH decreased to 3.5, a few branches start to grow (Fig. 8f) and these branches are monodisperse, aligned needles (Fig. 8g). Further decreasing the pH value stimulated the branch growth in both density and diameter, while the size of the central stem has a significant reduction. Multilevel structures with tertiary branches are observed (Fig. 8h) when the pH value is 3.3. In the present system, tree-like branched structure were formed by nucleation and growth of branches on the primary stems, which grown perpendicularly on the Nb substrate. When the critical pH value is reached, light surface etching induces nucleation of a polycrystalline layer by increasing the surface energy and creating nucleation sites, and these nuclei grow into oriented nanowires as the reaction continued. This kind of thin film can be produced with several square centimetres.
4.2 Non-equilibrium inter-diffusion induced tube formation

Hollow structures have emerged as an intriguing class of materials because of their high surface area and high porosity [31]. Based on the Nb_2O_5 nanostructures obtained in the former part, different tubular structures can be fabricated via a series of conversions. The formation of Nb_2O_5 nanotubes is demonstrated employing Nb_2O_5 nanorods as starting material. The void generation process is observed to be induced by phase transition between Nb_2O_5 polymorphs, leading to the formation of nanotubes [32].

The phase transformation of Nb_2O_5 was conducted by treating H-Nb_2O_5 nanorods in a solution containing LiOH and ethanediame at high temperature. As the H-phase is unstable at such circumstance, it will transform into M-phase Nb_2O_5 which is most stable from thermodynamical viewpoint (XRD characterization was carried out to confirm the phase transition process, identified the precursors and products as H-Nb_2O_5 and M-Nb_2O_5, see details in reference [32]). During the Nb_2O_5 phase-transformation process, non-equilibrium inter-diffusion is involved analogous to the Kirkendall effect, leading to the H-Nb_2O_5-M-Nb_2O_5 core-shell structure, and hollow M-Nb_2O_5 nanotube arrays can be finally obtained with elongated reaction time. Fig. 9 illustrates the tubular structure formation process. As shown in Fig. 9a, the precursor H-Nb_2O_5 is well aligned nanorod array which grew perpendicularly to the niobium substrate. Fig. 9b displays SEM image captured from a sample obtained at a reaction period of 6 h, the phase transition is observed to initially occur on the surfaces of the H-Nb_2O_5 nanorods, producing a thin layer of M-Nb_2O_5 on the H-Nb_2O_5 rod, small voids can be observed between H-Nb_2O_5 core and M-Nb_2O_5 shell, indicating condensation of vacancies at the boundary. Since the shell grows at the expense of core materials, with reaction time elongated to 12 h, the core and shell were observed to get separated by a clear gap as revealed by the difference in contrast visible in the SEM image of Fig. 9c. As the reaction proceeds, more H-Nb_2O_5 core materials diffuse out to the shell and the accompanying transport of vacancies leads to the merging and growth of voids, forming hollow M-Nb_2O_5 nanotubes (Fig. 9d).

![Fig. 9 Transformation form a) H-Nb_2O_5 nanorods to b, c) H-Nb_2O_5-M-Nb_2O_5 core-shell structure and finally to d) M-Nb_2O_5 nanotubes. Scale bar = 1 μm.](image)

4.3 Ligand-tuned-morphology of LiNbO_3

The solvent coordination molecule template method is well accepted to be an efficient pathway to fabricate materials with various shapes, since special structures and fascinating self-assembling characteristics of these organic ligands allow them to serve as templates for the design and preparation of complicated structures. In a designed ligand-assisted aqueous solution system for deliberately fabricating LiNbO_3 with controllable structures, SEM analysis was used to determine how amine ligand can effect on nucleation and growth of LiNbO_3 products [33].

For instance, shape-controlled synthesis of LiNbO_3 products can be achieved through deliberately selecting different amine ligands. The hydrothermal reaction between niobic acid and lithium hydroxide in ethylenediamine-water solution leading to the formation of LiNbO_3 rods, as can be seen in Fig. 10a, these rods are uniform in size with a diameter about 800 nm and length about 3 μm. By replacing ethylenediamine with n-butylamine, hollow spheres were obtained, with diameters of about 1.5–2 μm (Fig. 10b). From the triethylamine-assisted reaction system, the formed particles are monodisperse spheres with diameters of about 400 nm (Fig. 10c). The use of ethanolamine-water also prefers LiNbO_3 rod formation, which is similar in shape to those obtained in ethylenediamine-water system (Fig. 10d). The constructed spherical and rodlike structure may be dependent on the special properties and geometries of different amine ligands. n-butylamine is a monodentate ligand, while the geometry of triethylamine is complex and displays strong steric hindrance, ethylenediamine and ethanolamine are bidentate ligands and, moreover, their structures are almost identical. Ethylenediamine and ethanolamine can direct rodlike structure growth, mainly because they have multiple chelating sites in each molecule, which can induce LiNbO_3 to crystallize into 1D structure. The SEM observation of this ligand-tuned-morphology phenomenon will promote a better understanding of the role of organic additives in crystal growth.
5. Summary and Outlook

We have demonstrated that SEM is a modern, fundamental and well-suited investigative tool in the characterization of micro- and nanostructured materials. In addition to its main ability to offer a 2D visualization of large areas of the sample, SEM can also provide diversified qualitative and quantitative information on many physical properties including the size, morphology, surface texture, roughness, and chemical composition of materials. Moreover, advanced manipulation of the samples during the SEM experiments can provide key information about the morphology of the crystals at the micro- and nanometer scale, as well as insights into the different reaction pathways. In addition to materials characterization, SEM can also be integrated with some advanced accessories to perform in situ nanomaterial engineering and fabrication. Some examples of this integrated technology include nanomanipulation, electron beam nano-lithography, and focused ion beam techniques. Although these techniques are still unsophisticated, they should have important application in a variety of material research areas.

![SEM images of LiNbO$_3$](image)

**Fig. 10** SEM images of LiNbO$_3$ a) nanorods, b) nanospheres, c) hollow spheres and d) nanorods. The 1 µm bar applies to SEM images a, c and d). The bar in b is 4 µm.

Although SEM technique has been well developed in the past decades, there are still some shortcomings which limited their application. For example, samples subjected to SEM analysis must be conductive, although nonconductive samples can be coated with a thin layer of conductive materials, it might cause artifacts on samples. Traditional SEM also requires high vacuum test environment, although the development of environmental SEM allowing operation at higher pressure, the resolution of these devices are relatively limited. The damage to tested materials caused by the electron beam scanned across sample surface is another problem need to be considered, which could make the observation varies from time to time. With these problem solved by the advancing of SEM technology, a great more opportunities will be open to the material scientist.

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**References**


