Large-scale oxide nanostructures grown by thermal oxidation

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Abstract. Large scale oxide nanostructures of CuO, Fe₂O₃, Co₃O₄, ZnO, etc. were prepared by catalyst-free thermal oxidation process in atmosphere using pure metal as the starting material. Various single crystalline nanostructure arrays, including nanowires, nanobelts, nononeedles, nanoflakes, and nanowalls were obtained. These nanostructures can be grown from bulk materials, like foils or sheet, or from the microsized metal powders and the pre-deposited metal film. The growth time, temperature and substrate have important effects on the morphology, size and distribution of the nanostructures. Different from V-S or V-L-S mechanisms, the growth of nanostructure is found to be based on the metal ion diffusion process. The gradual oxidation process of the metals was clearly demonstrated. The properties of these nanostructures including gas sensing, magnetism, photoluminescence, and field emission were extensively investigated.

1. Introduction
Nanostructures with large surface area and possible quantum-confinement effect exhibit distinct mechanical, electronic, magnetic, optical and thermal properties. Some of the most important candidates in the family of nanomaterials are metal oxide nanostructures, which have great potential in addressing some fundamental scientific issues on low dimensionality and applications thereof. Oxide nanostructures can be grown by various methods such as chemical routes, template ways and by electro-spinning techniques. Future applications in commercial devices require further development of the growth method with the advantages of mass-production, efficiency, controllability, and catalyst-free. In addition, it should be able to synthesize the materials at relatively low temperatures, and to assemble the nanomaterials onto various substrates for further characterization and applications [1].

As early as the 1950s, the Cu, Fe, Zn, Ni and Mn oxides whiskers or filaments were prepared by annealing the corresponding metals in air at specific temperatures [2,3]. Currently, the thermal annealing method has been well developed and attracted much more attention due to its simplicity, low cost, and use of standard equipment. This synthesis can be carried out without a catalyst and sometimes even without any gas control. Such a chamber free approach is suitable for future large-scale production and for a variety of metals. In addition, the growth temperature for this technique is much lower than that used in normal vapor-based method. However, a clear understanding of the growth process and the properties of the nanostructures is still in need. In our recent work, various oxide nanostructures were synthesized by thermal oxidation and a systematic study on the growth and functional properties were carried out.
2. Synthesis of metal oxide nanostructures by thermal oxidation
Thermal oxidation methods can grow the metal oxide nanomaterials directly on the surface of bulk metals like foils, plates, or wires, as well as on the thin film or nanoparticles prepared by other processes. The purity, grain size and surface roughness of the precursors have effects on the nanostructure growth. The temperature, typically between 300 to 800°C, is a key factor governing the growing process, which can be provided by hot plate, furnace, oven or other alternative heating systems such as flame, resistive heating. Various heating sources can provide different temperature ramp rates from about 5°C/min to 100°C/s. The oxidation time can be varied from a few seconds to dozens of hours or more in some case. The oxidizing atmosphere can be dry or wet air, pure oxygen, a mixture of oxygen with argon, nitrogen, water vapor, etc. and it can be static or flow through the oxidation system. In addition, the background pressure can be ambient atmosphere or less than 1 atm, which also affects the growth process. The simplest thermal oxidation is heating the starting metals in air. The typical set-up of our hot-plate technique for thermal oxidation is shown in Fig.1. Various nanostructured oxides have been prepared from bulk, powder and film precursors.

![Figure 1. The preparation of oxide nanostructures by hot-plate technique and the facility](image)

2.1 CuO nanowires
CuO is a p-type semiconductor with a narrow band gap of 1.4 eV, and is also an antiferromagnetic material. It has been used as a basic material in high-$T_c$ superconductors and also has potential application in solar cells, field emission emitters, electronic cathode materials, catalysts and gas sensors [4-6]. Using the hotplate technique, we have grown single crystalline CuO nanowires with good quality [7], as shown in Fig.2. Typically, the nanowires were synthesized by heating copper in various forms at 400~500°C in air for 24-96 h. It was found that the growth temperature has a distinct influence on the diameter, while the growth time has an important effect on the length and density of nanowires (Fig.3). Kumar et al.[8] also obtained similar results, which are related to the growth mechanism. The substrate can also affect the nanostructure growth, as shown Figs.2. The different morphologies were obtained for the oxidations of Cu foil, grid, powders and film. Love et al. [9] prepared the CuO nanowires by heating the Cu powders with average particle sizes of 1, 10 and 50μm in a box furnace and found that the nanowire coverage also depends on the particle size.

![Figure 2. CuO nanowires synthesized by thermal oxidation: (a) a single nanowires; (b) nanowires on Cu grid; (c) nanowires on Cu foil (450°C); and (d) nanowires on Cu plate at 480 °C](image)
2.2 Fe₂O₃ nanowires, nanoneedles and nanoflakes

Hematite (α-Fe₂O₃) is another important semiconductor metal oxide with small band gap (E₉=2.1 eV), high corrosion resistance and low cost. Yu et al. [10] synthesized large scale α-Fe₂O₃ nanoflakes by heating the Fe foil in air using a hotplate. All flakes grew perpendicularly to the surface of the foil and have very sharp tips with mean diameter of 17 nm. Most nanoflakes are single crystalline with growth direction of [110]. The temperature has a distinct influence on the morphology. Zheng et al. [11] also synthesized ultra-sharp α-Fe₂O₃ nanoflakes on the hotplate at a very low temperature of 260°C and found that the nanoflakes become broader with increasing temperature. Three-dimensional urchin-like α-Fe₂O₃ structures were also formed via the thermal oxidation of Fe powders in air at ~280 to 480°C [12]. We prepared α-Fe₂O₃ nanostructures on Fe foils, powders and films (Fig.4) and found that the heating temperature, duration, substrate and the form of the precursor have important effects on the morphology, size and distribution of the nanostructure [13]. For the nanostructured grown on foil, it was found that there was wire-like structures at the low temperature (<430°C), flakes-like structures at 480°C, and no noticeable nanostructure coverage above 530°C. The obtained nanostructures were demonstrated single crystalline.

2.3 Co₃O₄ and MnO₂ nanostructures

The Co₃O₄ nanostructures have also been synthesized by direct heating the cobalt foils in air conditions. Yu et al. [14] prepared Co₃O₄ nanostructures by directly heating Co foil on a hotplate in ambient conditions at 200-350°C for 1min to 12h. They obtained single-crystalline Co₃O₄ nanowalls with several to tens nanometers in thickness and hundreds nanometers in length. They suggested that the morphology of the nanowall be controlled by the growth temperature and duration. We also synthesized Co₃O₄ and MnO nanowall or nanoflakes on Co and Mn foils, but no 1-dimensional nanostructures were observed (Fig.5).
2.4 Other oxide nanostructures

ZnO nanowires were also successfully synthesized by oxidation zinc foils, films in air [10,15]. We oxidized granular sputter deposited Zn films at 450-600°C [16] and ZnO nanowires were found to grow from individual Zn nanograins. Results showed that the nanowires preferably grow from relatively porous Zn film and a small amount of oxygen flow has beneficial effect. The single crystal nanowire obtained at 600 °C had a mean diameter of <50 nm with good structural quality.

Excepting the nanostructures of the monary metal oxide nanostructure, the hybrid nanostructures can also be produced when the precursors of binary alloys are employed. Zhu et al. [15] synthesized ZnO/CuO hybrid nanostructures by directly heating Cu-Zn alloy (brass) on a hotplate in ambient condition. With the increase in Zn concentration in brass, the dominant products transition from CuO nanowires to ZnO nanostructures. Both CuO and ZnO nanoflakes are obtained from the brass substrates with the intermediate ZnO content. It is worth noting that although CuO and ZnO are formed simultaneously on the same substrate, doping of Cu in ZnO or Zn in CuO was observed. Hence, this technique has potential to provide preparations for complicated oxide nanomaterials.

3. The growth mechanism for thermal oxidation process

The morphology and crystalline structure of the as-prepared oxide nanostructures are determined by the crystalline structure, purity, grain size, surface roughness of the starting metal. Also, the reaction parameters, such as temperature, atmosphere composition, oxygen partial pressure, heating systems, have significant effects. To control the growth of oxide nanostructures for various applications, their growth process and growth mechanism have to be fully understood. Numerous observations have been performed and have led to different theories regarding to the mechanisms for the spontaneous oxide nanostructure growth via thermal oxidation.

1D metal oxide nanostructures growth is usually described by either VS or VLS mechanism [17]. In VS process, the key steps are the evaporation of the precursor at high temperature followed by condensing of vapour and growth of the nanostructure in low temperature region. However, the temperature for thermal oxidation (typically 300-800°C) is far less than the melting points of the metals and their oxides, and the low and high temperature regions are difficult to distinguish. In VLS process, nanostructures grow with a catalyst (metal droplet) at the tip and the diameter of the structure determined by the size of the metal droplet is uniform. However, no metal catalyst droplet was observed in the experiments and the diameter of the nanostructures decreased from bottom to tip. Therefore, both VS and VLS mechanisms should not be responsible for the thermal oxidation growth.

We investigated carefully the structure and growth of various oxide nanostructures based on our hot plate technique. X-ray diffraction investigations showed various products obtained for oxidizing each metal. During thermal oxidation of Cu, both Cu2O and CuO were observed. For the oxidation of Fe, both Fe3O4 and Fe2O3 were also obtained. TEM results showed that the nanowires are single phase of CuO or Fe2O3. The cross-section of the oxidized product was investigated by FESEM with energy dispersive X-ray spectroscopy (EDS). A three layer structure of Cu2O film/CuO film/CuO nanowires for obtained sample is finally established for thermal oxidation of Cu, as shown in Fig.6a. The oxidation process of Cu includes two steps, i.e. 4Cu+O2→2Cu2O and 2Cu2O+O2→4CuO. Based on the Cu-O phase diagram, both CuO-Cu2O and Cu2O-Cu phase equilibriums exist at high temperature.
The equilibrium oxygen pressures at CuO-Cu₂O and Cu₂O-Cu interfaces, \( P_{\text{CuO-Cu}_2\text{O}} \) and \( P_{\text{Cu}_2\text{O-Cu}} \), can be calculated thermodynamically according to the equation

\[
P_{\text{equilibrium}} = \exp\left(-\frac{2\Delta G_0}{RT}\right),
\]

where \( \Delta G_0 \) is the free energy of formation of CuO or Cu₂O, \( R \) the gas constant (8.31 J/mol K) and \( T \) the absolute temperature. Based on the values of \( \Delta G_0 \) for Cu₂O and CuO [18], \( P_{\text{CuO-Cu}_2\text{O}} \) and \( P_{\text{Cu}_2\text{O-Cu}} \) can be given by \( 3.2\times10^{-7}–1.6\times10^{-3} \) and \( 3.3\times10^{-17}–1.7\times10^{-10} \) atm, respectively, in the temperatures range of 400-500 °C. The environmental oxygen partial pressure (0.21 atm) is higher than \( P_{\text{CuO-Cu}_2\text{O}} \) and \( P_{\text{Cu}_2\text{O-Cu}} \). Therefore, both CuO and Cu₂O can be formed in the present case. Thermodynamically, the CuO phase will be formed in the late stage of the oxidation due to the difference in above two equilibrium oxygen partial pressures. Indeed, from the experimental observation, the Cu₂O phase is the main product during the first stage of the thermal oxidation of copper, whereas the Cu₂O-CuO phase equilibrium becomes important afterwards. In addition, it has been suggested that several oxides including copper oxide formation follows a parabolic law [19], i.e., \( \ell^2 = k \cdot t \), where \( \ell \) is the thickness of CuO film, \( k \) is growth rate, and \( t \) is the time. If we consider the thickness as the nanowire length, from Fig. 3, the obtained values for the growth rate constant, \( k \), were about \( 3\times10^{-15} \text{ m}^2/\text{min} \) for \( T=430^\circ\text{C} \), which indicates that the growth of nanowire prepared by thermal oxidation follows the same mechanism that control the copper oxide film formation.

Very recently, Gonçalves et al. [20] proposed that the CuO nanowires are formed as a result of rapid, short-circuit diffusion of the Cu ions across grain boundaries and/or defects in a Cu₂O underlayer. Based on their proposal and our experimental results, a proposed nanowire growth model is given in Fig. 6c [7]. Initially a Cu₂O layer is formed, and due to the interface compressive stress such layer is highly porous and defective. Further oxidation requires that Cu atoms reach the film/air interface by two pathways: lattice and grain-boundary diffusion. The first pathway leads to a continuous increase of the Cu₂O and CuO layers, whereas the second results in the formation of the nanowires. The time dependence of the nanowire length, observed in Fig. 2 from 400 to 470 °C, can be directly attributed to grain-boundary diffusion of Cu ions toward the Cu₂O-CuO interface since the variations in the nanowire densities and diameters during growth at various temperatures are small. The morphology of the nanowires is determined by the microstructure of the underlying Cu₂O layer because it is within this intermediate layer where the “short-circuit” diffusion of Cu atoms takes place. Similarly, for oxidation of Fe or Co, Fe → Fe₃O₄ → Fe₂O₃ or Co → CoO → Co₃O₄ were demonstrated by both theoretical and experimental results. The cross section image of oxidized Fe is shown in Fig.6b.

Figure 6. Cross section SEM images for the Cu and Fe oxides (a, b) prepared by thermal oxidation and the schematic for thermal oxidation mechanism (c).

4. Properties and applications of the nanostructures

4.1 Gas sensing properties

A very simple gas sensor prototype was built in this work [7], shown in Fig. 7a. The CuO nanowires together with CuO and Cu₂O underlayers were used as the sensing materials. The current provided by a stable power resource was introduced through two silver electrodes from the top and bottom of the sample. This sensor was used to test ethanol concentrations of 50-1000 ppm at 100 °C. Fig. 7b shows
the resistances at various times for several ethanol concentrations. It indicates that the gas sensor has a very short reaction time, typically less than 30s. The resistance increases drastically with the increasing ethanol concentration. For a resistance of ~0.12 KΩ in air, when the ethanol concentration increases from 50 to 1000 ppm, the resistance increased from ~50 to >500 KΩ. By removing the sensor from ethanol atmosphere, it is found that, for a concentration of 1000 ppm, recovery time is less than ~120 s. The testing results are also found repeatable and reliable. As we know, CuO is a p-type semiconductor, and the electron injection emanated from the reaction between the reducing gas and the negatively charged surface oxygen increases the sensor resistance by decreasing the major charge carrier (hole) concentration. The high sensitivity of the prototype in a wide range of ethanol concentration makes it very practical for applications in many fields. For example, our prototype are very good for drunk driving detection working at ethanol concentration range of 200–800 ppm. Similarly, we have found that the Fe₂O₃ nanowires are also suitable for gas sensor with high sensitivity.

4.2. Magnetic properties

The magnetic properties of the prepared Fe₂O₃, Co₃O₄ and MnO nanostructures have also been investigated. As we all know, the Morin transition is a magnetic phase transition in α-Fe₂O₃ hematite where the antiferromagnetic ordering is reorganized from being aligned perpendicular to the c-axis to be aligned parallel to the c-axis below TM. A change in magnetic properties takes place at the Morin transition temperature. Fig.9 shows the $M(T)$ curves of α-Fe₂O₃ nanowires measured in the temperature range of 5-300K. The transition temperatures of 131 and 126 K were observed for the nanowires prepared at 430 and 480°C, respectively, which are much lower than $T_M = 263$ K for the bulk α-Fe₂O₃. Similar results have been found by other researchers [21,22]. It has been suggested that the reduction in $T_M$ in the hematite nanostructures result from lattice strain and defects [21] or uncompensated surface spins and/or shape effects of the nanowires [22].
4.3. Optical properties

The optical properties of ZnO nanowires have been well studied. Here we investigated the photoluminescence of α-Fe₂O₃ nanowires. As we know, in bulk α-Fe₂O₃, there is no PL due to magnetic and thermal relaxations, but in nanostructures, PL may occur for quantum confinement effect, the reduction of hyperfine-field or magnetic interactions, and the self-trapped state formation due to the enhanced electron–phonon interactions [23]. Zou et al. observed strong photoluminescence in Fe₂O₃ nanoparticles with size less than 20 nm [23]. A PL peak at 578 nm (2.14 eV) was also evident for α-Fe₂O₃ nanowires by Han et al. [24] Fig.9 shows the PL spectra for α-Fe₂O₃ nanowires synthesized on Fe foils at different temperatures under the 400 nm line excitations. Different from previous work, a PL peak at 791~795 nm (~1.56 eV) was found. Since the band gap of bulk α-Fe₂O₃ is 2.10 eV, the appearance of the peak in infrared light range indicated an unclear mechanism. Generally, the PL of 1-D α-Fe₂O₃ results from the enlarged Fe–O bond, which leads to magnetic coupling of neighbouring Fe³⁺ ions. Fig.9 also show that the samples prepared at 380°C and 430°C with different morphologies have significant different PL intensities, which is related to the size dependent quantum confinement effect, since the sample prepared at 380 has shown high length/width ratio.

\[ \text{Figure 9. PL spectrum of } \alpha \text{-Fe}_2\text{O}_3 \text{ nanowires synthesized on (a) Fe foils at different temperatures} \]

4.4 Field emission

The 1-D nanomaterials are suitable for field emission. We tested the field emission properties of α-Fe₂O₃ nanoneedles obtained by hot plate technique under a vacuum of 5.1×10⁻⁵ Pa. Fig.10 shows the structures and current density vs electric field curves. The nanoneedles prepared on Fe foil has the threshold field of 14.5 V/µm corresponding to the current density of 10 µA/cm². The current density is 17.4 µA/cm² when the electric field is 16.20 V/µm. The nanoneedles prepared on Fe/Si substrate has the threshold field value of 13.3 V/µm corresponding to the current density of 10 µA/cm². For the nanoneedles prepared on the Fe/ITO substrate, relatively low threshold field of 9.3 V/µm was obtained. Rackauskas et al. [25] investigated various nanowires produced by thermal oxidation and found the CuO nanowires showed the best FE characteristics. The threshold field value corresponding to the current density of 0.01 mA/cm² was ~4 V/µm. The maximum current density was ~100 mA/cm².

\[ \text{Figure 10. } \alpha \text{-Fe}_2\text{O}_3 \text{ nanoneedles on Fe foil (a) and film (b), current density vs electrical field curves (c)} \]
5. Summary
The nanostructures of metal oxides including CuO, α-Fe2O3, Co3O4, ZnO etc. have been synthesized via thermal oxidation. This process is very simple, cost-effective and suitable for mass production in large-scale applications. The nanostructures can be grown on the surface of bulk metals, as well as the thin film or nanoparticles. The heating temperature and composition of the oxidizing atmosphere have distinct effects on the morphology and structure. The length can be determined by the thermal duration, whereas the diameter can be determined by the substrate temperature. The VS and VLS mechanism cannot explain the thermal oxidation growth process and a short-circuit diffusion mechanism was proposed. In addition, the grown nanostructures show some interesting physical properties and have potential applications for magnetic, optical, field emission and gas sensing devices. It is expected that new oxide nanostructures with more complicated structure and composition and novel properties may also be produced by this simple process.

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7. References
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