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<td>Pan, Jun; Shen, Hao; Mathur, Sanjay</td>
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Review Article

One-Dimensional SnO₂ Nanostructures: Synthesis and Applications

Jun Pan,¹,² Hao Shen,¹ and Sanjay Mathur¹

¹ Institute of Inorganic and Materials Chemistry, University of Cologne, 50939 Cologne, Germany
² Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371

Correspondence should be addressed to Jun Pan, jun.pan@hotmail.com

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Nanoscale semiconducting materials such as quantum dots (0-dimensional) and one-dimensional (1D) structures, like nanowires, nanobelts, and nanotubes, have gained tremendous attention within the past decade. Among the variety of 1D nanostructures, tin oxide (SnO₂) semiconducting nanostructures are particularly interesting because of their promising applications in optoelectronic and electronic devices due to both good conductivity and transparency in the visible region. This article provides a comprehensive review of the recent research activities that focus on the rational synthesis and unique applications of 1D SnO₂ nanostructures and their optical and electrical properties. We begin with the rational design and synthesis of 1D SnO₂ nanostructures, such as nanotubes, nanowires, nanobelts, and some heterogeneous nanostructures, and then highlight a range of applications (e.g., gas sensor, lithium-ion batteries, and nanophotonics) associated with them. Finally, the review is concluded with some perspectives with respect to future research on 1D SnO₂ nanostructures.

1. Introduction

One-dimensional (1D) nanoscale materials, such as nanotubes, nanowires, and nanobelts, have attracted significant attention due to their unique size- and dimensionality-dependent electrical, optical, chemical, and mechanical properties and promising applications as interconnection and functional components in designing nano-sized electronic and optical devices [1, 2]. 1D semiconductor nanostructures represent an important and broad class of nanoscale wire-like structure, which can be rationally and predictably synthesized in single crystalline form with controlled chemical composition, diameter, length, and doping level with high precision. The availability of nanostructures has enabled a wide-range of proto-type devices and integration strategies [3, 4].

It is well known that materials behave differently at the nanoscale than their bulk counterparts. Low-dimensional nanoscale materials, with their large surface areas and possible quantum confinement effects, exhibit superior mechanical, thermal, chemical, electrical, and optical properties distinct from their bulk counterparts. The manipulation of well-controlled precise dimensions, crystallinity, and composition of 1D nanostructures gives rise to unique properties, thus enabling a variety of applications that would not be possible with materials with bulk dimensionality. Doubtlessly, a thorough understanding of the fundamental properties of the 1D nanostructures system is indisputably the prerequisite of research and development towards practical applications [5].

As a n-type direct wide-band semiconductor (\(E_g = 3.6\) eV at 300 K), SnO₂ is transparent in the visible light region and useful as optoelectronic devices [6], catalyst supports [7], transparent conducting electrodes [8], antireflective coatings [9], and a proto-type material for metal oxide sensors [10]. One-dimensional tin oxide nanostructures have been synthesized by a variety of techniques, including vapor transport [11], carbothermal reduction [12], laser ablation of pure tin in an oxidizing Ar/O₂ atmosphere [13], oxidation of electrodeposited tin wires [14], oxidation of tin vapors at elevated temperatures [15], solvothermal synthesis [16], and electrospinning [17], and so forth. Our group reported a molecule-based chemical vapor deposition (MB-CVD) to synthesize 1D SnO₂ nanowires [18, 19], nanowire arrays [20, 21], and heterostructures [22] by the decomposition
of a single-molecular precursor \([\text{Sn(O'Bu)}_4]\) containing preformed Sn-O bonds on gold nanoparticles, on a Si, Al$_2$O$_3$, and TiO$_2$ substrates via the well-known vapor-liquid-solid (VLS) growth mechanism. Meanwhile it is precisely controlled over chemical composition, morphology, and deposition rate.

This article will provide a helpful review of the state-of-the-art research activities focused on synthesis and devices of 1D SnO$_2$ nanostructures. The first section introduces typical 1D nanostructures obtained on SnO$_2$, including nanowires, nanotubes, nanobelts, and some special nanostructures. Next, some important electronic and optoelectronic devices built on 1D SnO$_2$ nanostructures are presented, which include gas sensor, lithium-ion batteries, and nanophotonics. This review will then conclude with some perspectives and outlook on the future developments in the 1D SnO$_2$ nanostructures and related research areas.

2. Typical 1D SnO$_2$ Nanostructures

2.1. Nanowires. SnO$_2$ nanowires have been synthesized by several physical and chemical methods, for example, vapor-solids (VS) synthesis by SnO evaporation under pulsed flow conditions led to the formation of segmented wires [23]. In addition, thermal evaporation of SnO or SnO$_2$ was also used to the formation of nanowires in high quantity [24]. Furthermore, SnO$_2$ nanowires have been obtained by self-catalyzed growth mechanism via carbothermal synthesis [25], the laser ablation of pure tin in oxidising Ar/O$_2$ atmosphere [13], and oxidation of electrodeposited tin wires within structure directing AAO membranes [26] or through oxidation of tin vapours at elevated temperatures [15]. The catalyst-assisted molecule-based CVD growth is a generic approach towards controlled synthesis of metal oxide nanostructures and had been demonstrated for SnO$_2$, as shown in Figure 1. It is revealed that the average radial dimension of the SnO$_2$ wires is approximately 0.9–1.1 \(\mu\)m. The indexing of the SAED pattern shows that the SnO$_2$ nanowires grow along the [100] direction with an interplanar spacing of 0.334 nm, which corresponds to the \{110\} plane of SnO$_2$ in the rutile phase [18]. Large surfaces covered with tin oxide nanorods could be achieved by an aqueous approach controlling ionic strength and pH of precursor solutions [27].

2.2. Nanotubes. Considerable attention has also been paid to semiconducting nanotubes due to high surface-to-volume ratios compared with their solid wire counterparts since the first report of carbon nanotubes by Iijima in 1991 [28]. Nanotubes are often obtained for materials with layered or pseudolayered structures [29]. For the preparation of SnO$_2$ tubular structures, the template-assisted approach has been proven to be an effective route, which generally involves the use of removable templates, such as preobtained nanorods [30], cellular fibers [31], porous membranes [32], and carbon nanotubes (CNTs) [33]. However, the morphologies of the tubular structures are rather limited due to the difficulty in fabricating templates with diverse morphologies. Recently, 1D silica mesostructures are used as sacrificial templates to synthesize SnO$_2$ nanotubes with preserved morphologies via a simple hydrothermal route (Figure 2(a)), resulting in the formation of well-defined SnO$_2$ nanotubes with different lengths and unique helical SnO$_2$ nanotubes with a wealth of conformations (Figures 2(b) and 2(c)) [34]. In addition, SnO$_2$ nanotubes with controlled diameter and length were synthesized using an electrochemical method at room temperature. The length and wall thickness of the nanotubes increased monotonically with the deposition time, and the diameter of the nanotubes was altered by varying the pore size of the scaffolds [35].

2.3. Nanobelts. Nanobelts (or nanoribbons), an independent family in the realm of 1D nanomaterials, are regarded as an ideal system to fully understand dimensionally confined transport phenomena and may act as valuable units to construct nanodevices owing to their well-defined geometry [36]. SnO$_2$ nanobelts have been successfully synthesized by thermal evaporation of different source materials. Structurally perfect and uniform single crystalline SnO$_2$
nanoribbons, with widths of 30–200 nm, width-to-thickness ratio of 5–10, and length of several hundred micrometers to a few millimeters, were synthesized by simple thermal evaporation of SnO$_2$ or SnO powder at high temperatures. It is worth to notice that wire-like nanostructures can be observed in the first stage of growth process due to the presence of strain. The profile of the fringes implies that the geometrical shape of wire-like nanostructures is likely to be a ribbon [37]. SnO$_2$ nanobelts also were synthesized by mixture of Sn foil and SnO powders with the same growth mechanism [24]. A simple rapid oxidation of elemental tin was proposed for large-scale production of SnO$_2$ nanoribbons. The width of the nanostructure was sensitive to the reaction temperature. When the growth temperature was increased to 1350°C, the diameter range of these nanostructures increased markedly to 50–350 nm (Figure 3(b)) compared to the wire-like nanostructures grown at 1080°C (Figure 3(a)). The lengths of the nanoribbons were up to several hundreds of micrometers, and the typical width and thickness were in the range of 30–150 nm and 10–30 nm (Figure 3(c)), respectively. The as-synthesized SnO$_2$ nanoribbons appeared to be single crystalline and exhibited [110] and [203] growth directions (Figures 3(d)–3(e)) [38]. Recently, {101} surfaces of zigzag SnO$_2$ nanobelts have been synthesized by a VS process, which are reduced surfaces terminated by Sn atoms and the Sn terminated surface is a nonpolar surface. As both reduced SnO and stoichiometric SnO$_2$ (101) surfaces are neutral terminations, the polar surface model is no more suitable for the (101) type surface of rutile SnO$_2$ nanobelts [39].

2.4. Other SnO$_2$ 1D Nanostructures. Synthesis and assembly of SnO$_2$ 1D nanostructures with special morphologies, shapes, and compositions have attracted great interests very recently because they process unique properties and functionalities that are not accessible in the single-component materials, due to the combination of material classes such...
Figure 3: SEM images of SnO$_2$ (a) wire-like nanostructures and (b) nanoribbons, and TEM images (c)–(f) of SnO$_2$ nanoribbons.

Figure 4: SEM and TEM images of SnO$_2$-$V_2$O$_5$ heterostructures.

The advantages of using 1D nanostructures for chemical sensing are diverse. With a large surface-to-volume ratio and a Debye length comparable to the nanowire radius, the electronic property of the nanowire is strongly influenced by surface processes, yielding superior sensitivity than their thin film counterpart. The sensing mechanism of metal oxides is mainly governed by the fact that the oxygen vacancies on the oxide surfaces are electrically and chemically active, therefore, the conductivity (or resistivity) of oxide nanomaterials is strongly affected by the adsorbed molecules. SnO$_2$ is n-type semiconductor with oxygen deficiency. The lattice oxygen is evaporated in the form of gas, which makes the doubly ionized oxygen vacancy and electrons. If tin dioxide is heated at 300–400 $^\circ$C, the oxygen in the atmosphere is adsorbed at the surface of SnO$_2$ with the negative charge. Because electron is provided from the surface of crystal, the surface of tin oxide becomes an electron depletion layer.

3. Applications of 1D SnO$_2$ Nanostructures

As an important group of wide-band gap semiconductors with tunable conductivity and high transparency, 1D SnO$_2$ nanostructures have been used to fabricate nanoscale gas sensor, electronic and optoelectronic devices.

3.1. Gas Sensor. Gas sensing using nanomaterials is an attractive, versatile application for important molecule species, environmental and security-checking purposes [44, 45].
This means the formation of potential barrier near the grain boundary. If CO is present in the atmosphere, the CO oxidizes into CO$_2$ with the reaction of adsorbed oxygen and remaining electron returns to the SnO$_2$ crystal. This increases the electrical conductivity to a great extent. So, we can detect CO by measuring the remarkable resistance decrease upon CO reaction. Generally speaking, the reduction in resistance occurs mainly at the surface and can be explained by the reduction of potential barrier [46].

The first SnO$_2$ nanobelt chemical sensor was made on an alumina substrate by dispersing SnO$_2$ nanobelts atop prefabricated platinum interdigitated electrodes on a substrate. The sensor was employed to detect CO and NO$_2$ for environmental polluting species and ethanol for breath analysis. A single-SnO$_2$-nanobelt sensor integrated with microheaters to sense dimethyl methylphosphonate (DMMP) was fabricated. The conductance of the SnO$_2$ nanobelt sensor was reduced by 5% when the sensor was exposed to 78 ppb of DMMP [47]. It was also reported that light photoactivates molecule absorption and desorption as an alternative way to the use of temperature. An explosive environment is the typical application where the use of heated sensors is not favorable. The strong photoconducting response of individual single-crystalline SnO$_2$ nanoribbons makes it possible to achieve equally favorable adsorption-desorption behavior at room temperature by illuminating the devices with a ultraviolet (UV) light of energy near the SnO$_2$ bandgap. The active desorption process is thus photoinduced molecular desorption [48]. Kolmakov et al. realized an array of parallel nanowires of SnO$_2$ by using self organized highly ordered porous alumina templates. Conductance measurements were performed on isolated individual nanowires with vapor-deposited Ti/Au microcontacts. They analyzed the behavior of nanowire in N$_2$ and N$_2$ + 10% O$_2$. CO reacts with preadsorbed oxygen species on SnO$_2$ to form carbon monoxide thus donating few electrons back into the bulk resulting in an increased conductivity, which depends monotonically on the gas phase partial pressure of CO (Figure 5) [14]. Single SnO$_2$ metal oxide nanowires are used at the nanoscale level as individual monocrystal for the electrical transduction of the gas interaction with these sensing materials. Electrical contact characteristics and resistance variations under different gas ambient are analyzed from two- and four-probe measurements of individual nanowires. CO and humidity behaviors are reported for single SnO$_2$ nanowires with CO detection threshold smaller than 5 ppm and measurement instability lower than 4% (Figure 6) [49]. A technical approach to fabricate practical devices by coupling a single-crystal SnO$_2$ nanowire sensing element with a microhotplate gas sensor platform was also presented [50].

In order to tune the sensitivity and selectivity of SnO$_2$ nanowires-based sensors, many techniques have been explored. The addition of a small amount of noble metals such as Au, Pd, Pt, and Ag and Ni speeds up surface reactions and improves selectivity towards target gas species [51]. Kolmakov examined the influence of the surface sensitization with catalyst particles of Ni/NiO and Pd [52]. Wan reported the use of Sb doping to tailor the resistivity of SnO$_2$ nanowires deposited by thermal evaporation process starting from a mixture of Sn and Sb powders in the ratio 10 : 1 [53]. Meanwhile, Pan et al. modified SnO$_2$ nanowires by Ar/O$_2$ plasma treatment through preferential etching of the lattice oxygen atoms, which produced nonstoichiometric surface compositions that imparted a many-fold higher sensitivity toward gas absorption on such surfaces (Figure 7) [54].

3.2. Anode Materials for Lithium-Ion Batteries. Rechargeable lithium-ion batteries (LIBs) have been recognized as
an attractive power source for popular mobile devices. At present, LIBs are efficient, light-weight, and rechargeable power sources for consumer electronics such as laptop computers, digital cameras, and mobile phones. Moreover, they have been extensively studied for use as power supplies of electric vehicles (EVs) and hybrid electric vehicles (HEVs), which require high energy and power densities [55].

As a promising anode material for LIBs, tin-based material has attracted growing attention owing to the extraordinary electrochemical behavior, such that the initial irreversible capacity induced by Li$_2$O formation, and the abrupt capacity fading caused by volume variation could be effectively reduced when in nanoscale form, the high theoretical capacity (992 mAh g$^{-1}$) and the higher operating voltage comparing to traditional carbonaceous anode active materials [56, 57]. The self-catalytically grown SnO$_2$ nanowires could provide more reaction sites on the surface and enhance the charge transfer in the electrochemical reactions. Moreover, Sn particles at the tips of nanowires also contributed to the Li$^+$ storage and prevented the capacity loss that is induced by the existing metal catalysts. SnO$_2$ nanowires showed an initial Coulombic efficiency of approximately 46.91% and improved cyclic performance and a higher reversible specific capacity of over 300 mAh g$^{-1}$ up to the 50th cycle as shown in Figure 8 [58]. In addition, SnO$_2$ nanowire
SnO$_2$ nanorod arrays represent an excellent geometry because they can offer direct channels for efficient electron transport. SnO$_2$ nanorod array electrodes can be produced in a one-pot template-free alkaline hydrothermal process. The array electrode showed good performance as a LIB anode in properties such as capacity retention (580 mAh$^{-1}$ after 100 cycles at 0.1 C) and rate capability (stable 350 mAh$^{-1}$ at 5 C) [60].

SnO$_2$ has recently been shown to act as an excellent subwavelength waveguide because of its defect-related PL bands at 2.5 eV (green) and 2.1 eV (orange) (Figure 10) [65]. Nonresonant waveguiding (i.e., subbandgap light) in these structures can be achieved by simply focusing laser diodes on the end facet of the nanowire. SnO$_2$ wires have dimensions between 100 nm and 400 nm, an optimal size range to efficiently guide visible and UV wavelengths because of the high index of refraction of SnO$_2$ ($n > 2$). Optical linkages between active nanowires (GaN and ZnO) and passive nanowires (SnO$_2$) can be formed via tangential evanescent coupling (Figure 11). It has been shown that a staggered side-by-side configuration, in which the active and passive elements interact over a few microns, outperforms bridged, or direct end-to-end coupling. Weaker coupling is achieved by staggering structures with a thin air gap (several hundred nanometers) between them, allowing communication via tunneling of evanescent waves [66]. With further integration, it should be possible to create more functional geometries, such as branched optical hubs and Mach-Zehnder interferometers (optical modulators) that use the electro-optic effect for phase shifting. The integration of high-frequency electrically driven lasers with passive nanowire waveguides is the next step toward effectively transducing and routing packets of optical information within an optical computer.
Figure 9: (a) Schematic diagram showing the strategy for coating V2O5 on SnO2 nanowires, and typical TEM images of a single SnO2/V2O5 core/shell nanowires, (b) the galvanostatic charge/discharge curves at different current densities, and (c) the cycling performance at different temperatures of the SnO2/V2O5 core/shell nanowires electrode tested.

or communication device [67]. However, the goal of room temperature, electrically driven nanolasers, remains an active area of current research.

4. Summary and Perspective

In summary, we provide a comprehensive review of the state-of-the-art research activities focused on rational synthesis (e.g., nanowires, nanobelts, nanotubes, and heterostructures) and potential applications (e.g., gas sensor, lithium-ion batteries, and nanophotonics) of 1D SnO2 nanostructures. The fascinating achievements, till now, towards the device applications of 1D SnO2 nanostructures should inspire more and more research efforts to address the remaining challenges in this interesting field in the future.

Controlled manipulation of matter at the nanoscale will lead to fascinating and novel behavior and also impact device properties. The ability to rationally control key 1D SnO2 nanostructures parameters during growth, fabricate intra-NW heterostructures with well defined [68], and atomically abrupt crystalline interfaces should further increase the versatility of 1D SnO2 nanostructure-based electronic and photonic devices and also reduce the load for subsequent assembly processes.

Such a synthetic control will be extremely useful for creating precisely defined systems to investigate the effects of quantum confinement on electronic and optical properties
Figure 10: Demonstration of absorption and fluorescence schemes using individual SnO$_2$ nanoribbon waveguides. (a) Dark-field photoluminescence image of the absorption scheme showing an analyte centered in the middle of the ribbon and the labeled excitation and collection locations. (b) Spectra recorded after the SnO$_2$ defect emission traversed through the ribbon in air (black), pure glycol (green), and 1 mM dye-loaded glycol (red). (c) Bright-field image of 2 $\mu$m yellow-green fluorescent polystyrene beads placed with an optical trap precisely on or near a SnO$_2$ nanoribbon. (d) Fluorescence image of beads after waveguiding of photoluminescence from the SnO$_2$ ribbon. Inset: false color expansion of bead 1 during UV excitation of the ribbon.

of nanostructures resulting from the modification of the electronic density of states and also aid in developing novel nanophotonic devices.

Looking into the future, with extensive research in nanostructures synthesis to accurately control dimension and composition, a critical understanding of the modified properties of materials at the nanoscale, and the hierarchical assembly of nanostructures with exquisite spatial control, progress will be made, and new and interesting nanosystems will create the technologies of the future.
Figure 11: (a) Dark-field image illustrating the coupling of two nanowire lasers (GaN and ZnO) to a common SnO$_2$ nanoribbon waveguide. Scale bar = 25 μm. (b) Spectra recorded at the left terminus of the SnO$_2$ nanoribbon after simultaneous nanowire laser injection.

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References


