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ZnO and ZnS Nanostructures: Ultraviolet-Light Emitters, Lasers, and Sensors

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ZnO and ZnS Nanostructures: Ultraviolet-Light Emitters, Lasers, and Sensors

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ZnO and ZnS, well-known direct bandgap II–VI semiconductors, are promising materials for photonic, optical, and electronic devices. Nanostructured materials have lent a leading edge to the next generation technology due to their distinguished performance and efficiency for device fabrication. As two of the most suitable materials with size- and dimensionality-dependent functional properties, wide bandgap semiconducting ZnO and ZnS nanostructures have attracted particular attention in recent years. For example, both materials have been assembled into nanometer-scale visible-light-blind ultraviolet (UV) light sensors with high sensitivity and selectivity, in addition to other applications such as field emitters and lasers. Their high-performance characteristics are particularly due to the high surface-to-volume ratios (SVR) and rationally designed surfaces. This article provides a comprehensive review of the state-of-the-art research activities in ZnO and ZnS nanostructures, including their syntheses and potential applications, with an emphasis on one-dimensional (1D) ZnO and ZnS nanostructure-based UV light emissions, lasers, and sensors. We begin with a survey of nanostructures, fundamental properties of ZnO and ZnS, and UV radiation–based applications. This is followed by detailed discussions on the recent progress of their synthesis, UV light emissions, lasers, and sensors. Additionally, developments of ZnS/ZnO composite nanostructures, including core/shell and heterostructures, are discussed and their novel optical properties are reviewed. Finally, we conclude this review with the perspectives and outlook on the future developments in this area. This review explores the possible influences of research breakthroughs of ZnO and ZnS nanostructures on the current and future applications for UV light–based lasers and sensors.

Keywords ZnO and ZnS nanostructures, ultraviolet light emissions, lasers and sensors, photodectors, photosensors or photoconductors, visible-light-blind ultraviolet light sensors, optical sensors, oxide, sulfide

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1. INTRODUCTION

Nanoscience and nanotechnology involve studying and working with matter on a nanoscale. Phenomena at the nanoscale are likely to be a completely new world, where properties may not be predictable from those observed at larger scales. The nanostructures’ small size allows them to exhibit novel and significantly modified physical, chemical, and biological properties, which are different from those of materials in the micrometer scale. The latter mostly exhibit the same physical properties as the bulk forms. Nanoscience and nanotechnology encompass a range of techniques rather than a single discipline and stretch across the whole spectrum of science, spanning medicine, physics, engineering, chemistry, and materials science. The ability to manipulate and process materials at the nanoscale with excellent reproducibility is vital to the advancement of manufacturing industry. “There’s plenty of room at the bottom, I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle. What I want to talk about is the problem of manipulating and controlling things on a small scale...”; this famous statement of legendary Richard Feynman made in 1959 at the annual meeting of the American Physical Society (APS) with immense foresight has been realized in less than half a century by consistent efforts and significant contributions from the scientific community across the globe. Nowadays, research on nanomaterials and nanostructures is not only among the most active fields in nanotechnology but it is also being gradually introduced into our daily life.\(^\text{3–10}\)

1.1. Nanostructures

Structures with at least one dimension between 1 and 100 nm are called nanostructures.\(^\text{11}\) Interest in the physics of condensed matter at size scales larger than those of atoms and smaller than those of bulk solids (mesoscopic physics) has grown rapidly since the 1970s, due to the growing understanding that the properties of these mesoscopic atomic ensembles are different from those of conventional solids, and their fascinating properties as well as novel characteristics should originate from their morphologies.\(^\text{12–20}\) For example, nanosized semiconductors (semiconductor clusters) have the potential to revolutionize the fields of photodetection and photocatalysis through the combined effects of quantum confinement and unique surface morphologies.\(^\text{21}\) As a consequence, interest in artificially
assembled materials from nanometer-sized building blocks arose because their properties can be altered by controlling the sizes in the range of 1–100 nm and the assembly of such constituents.\(^2\) There is a large number of new properties and applications that could be realized by reducing the size of currently existing structures into the nanometer scale (\(<100\) nm) or by making new types of nanostructures. The most successful examples are seen in microelectronics, where \textit{smaller} has always meant a greater performance ever since the invention of transistors; e.g., higher density of integration, faster response, lower cost, and less power consumption.\(^1\) Nanostructures are fundamental to nanoscience and nanotechnology and are expected to offer distinguished performance in future nanodevices.

Nanostructures are modulated over nanometer length scales in zero to two dimensions. They can be divided into zero-dimensional (0D when they are uniform), one-dimensional (1D when they are elongated), and two-dimensional (2D when they are planar) based on their shapes. The recent emphasis has been put on 1D nanostructures, perhaps due to the intriguing possibility of using them in a majority of short-term future applications since the identification of C nanotubes in 1991.\(^3\)

Nanotubes, nanowires, nanobelts, nanorods, nanocables, etc., are a new class of 1D nanostructures that have been attracting a great deal of research interest in recent years due to their unique properties and potential to revolutionize broad areas of nanotechnology.\(^4\)–\(^9\) Nanocircuits built using semiconductor nanowires were declared a “breakthrough in science” by \textit{Science} magazine.\(^10\) \textit{Nature} magazine published a report claiming that “Nanowires . . . it does not matter what you can call them, they are the hottest property in nanotechnology.”\(^11\) There is no doubt that 1D nanostructures will be the new focal point of research in coming years. For example, 1D inorganic nanostructures have been demonstrated as ideal systems for exploring a large number of novel phenomena at the nanoscale and investigating the size and dimensionality dependence of their properties for potential applications. The use of such nanostructures with tailored geometries as both interconnects and functional building blocks is also expected to play a crucial role in future nanodevices.\(^12\) Field-effect transistors (FETs) based on individual nanowires are ultrasensitive nanosensors for detecting a wide range of gases, chemicals, and biomedical species in both commercial and research applications. The high-performance characteristics are particularly due to high surface-to-volume ratios (SVR) and rationally designed surfaces.\(^13\)

Although 1D nanostructures can now be fabricated using a number of advanced nanoscale lithographic techniques, such as short-wavelength optical lithography, electron-beam (e-beam) or focused-ion-beam (FIB) writing, proximal-probe patterning, laser ablation, ion beam irradiation, nanoimprint lithography, etc.,\(^1\) many 1D nanostructures were synthesized by two major approaches based on the reaction media that were used during the preparation: solution- and gas phase–based processes.\(^14\) Solution-based approaches mainly rely on template-directed synthesis, solution–liquid–solid (SLS) methods, and solvothermal chemical synthesis. Gas phase–based processes for 1D nanostructures mainly include four growth mechanisms: vapor–liquid–solid (VLS) process, vapor–solid (VS) growth process, oxide-assisted growth, and a combination method of the anodic alumina membrane (AAM) and chemical vapor deposition (CVD).\(^15\) The details for these methods can be found in our previous paper.\(^16\)

\subsection*{1.2. Fundamental Properties of ZnO and ZnS}

Zinc oxide (ZnO) and zinc sulfide (ZnS), well-known direct bandgap II–VI semiconductors, are promising materials for fabricating photonic, optical, and electronic devices. From Table 1, one can easily see that both ZnO and ZnS have similar fundamental physical properties, including crystal structures, lattice constants, melting points, and so on.\(^17\) With wide bandgaps of \(\sim3.37\) eV for ZnO and \(\sim3.7\) eV for ZnS at room temperature (RT; \(3.72\) eV for cubic zinc blende [ZB] ZnS and \(3.77\) eV for hexagonal wurtzite [WZ] ZnS), ZnS, ZnO, and their compound/composite structures are unique candidates for ultraviolet (UV) light lasers and detectors working in the 320- to 400-nm wavelength range, naturally accessible at the Earth’s surface. Here, we provide a brief review on the fundamental properties and the current research activities of ZnO and ZnS nanostructures.

ZnO has a large exciton binding energy of 60 meV and is suitable for short wavelength optoelectronic applications.\(^18\) The high exciton binding energy in a ZnO crystal can ensure efficient excitonic emission at RT and such RT UV luminescence has indeed been reported in disordered nanoparticles and thin

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
     & \textbf{Lattice constants} & \textbf{Bandgap (eV)} & \textbf{Exciton binding energy (meV)} & \textbf{Work function (eV)} & \textbf{Melting point (K)} & \textbf{Positions of UV emissions (nm)} \\
\hline
\textbf{Crystalstructures} & \textbf{\(a\) (nm)} & \textbf{\(c\) (nm)} & & & & \\
\hline
\textbf{ZnO} & Hexagonal wurtzite & 0.3249 & 0.5207 & 3.37 & 60 & 5.3 & 2,248 & 368–390 \\
\textbf{ZnS} & Cubic zinc blende/ & 0.3823 & 0.6261 & 3.72/3.77 & 39 & 7.0 & 2,103 & 330–345 \\
\textbf{hexagonal wurtzite} & & & & & & & & \\
\hline
\end{tabular}
\caption{Comparison of some fundamental ZnO and ZnS physical properties}
\end{table}

Reproduced from Fang et al.\(^17\) Copyright \(\copyright\) 2008, \textit{JMST}.
films. Additionally, ZnO is transparent to visible light and can be made highly conductive by doping.\textsuperscript{36} Besides, the non-centro-symmetry in wurtzite and the polarity developed along the $c$ axis make this material inherently piezoelectric, which, in combination with its large electromechanical coupling, results in strong piezoelectric and pyroelectric properties useful in actuators, piezoelectric sensors, and nanogenerators.\textsuperscript{37–41}

On the other hand, ZnO is also a biocompatible material with a high isoelectric point (IEP) of $\sim 9.5$, which makes it suitable for adsorption of proteins with low IEPs, because the protein immobilization is primarily driven by electrostatic interactions. Moreover, ZnO nanostructures have unique advantages including high specific surface area, low toxicity, chemical stability, electrochemical activity, and high conductivity. Hence, they are a promising material for biosensor applications and can be directly used for biomedical applications without coating.\textsuperscript{42}

Since the 1960s, synthesis of ZnO thin films has been an active field because of their applications as sensors, transducers, and catalysts. Over the last decades, the synthesis of ZnO nanomaterials/nanostructures has been of growing interest due to their promising applications in nanoscale devices. ZnO exhibits the most splendid and abundant configurations of nanostructures that one material can form, and its electrical and optical properties depend sensitively on both the morphology and size. ZnO grows best on sapphire and GaN substrates because of the good lattice match but can also be grown on Si for more general usages.\textsuperscript{43} Numerous nanostructures have been synthesized via a variety of techniques; e.g., ZnO nanoarrays, nanorods, nanowires, nanobelts, nanoribbons, nanotubes, nanorings, nanohelices, nanobowls, nanotips, nanoflowers, nanobullets, nanosheets, nanomails or nanopencils, nanosprings, nanoplatelets, nanoporous structures, nanowalls, nanobridges, hierarchical nanostructures, etc.\textsuperscript{44}

Similar to ZnO, ZnS is another semiconductor that has been extensively studied. In nature, ZnS is a white- to yellow-colored powder or crystal.\textsuperscript{45} Both ZB and WZ structures of ZnS are covalently bonded solids. ZnS was one of the first semiconductors discovered and one of the most important materials in the electronic industry with a wide range of applications.\textsuperscript{46} As described in Wikipedia, ZnS was used by Ernest Rutherford and others in the early years of nuclear physics as a scintillation detector due to its unique property of emitting light upon excitation by X-rays or electron beams.\textsuperscript{45} At the same time, bulk ZnS with addition of a few parts per million (ppm) of suitable activator has been used as phosphor for cathode ray tubes using X-ray screens in dark conditions. Metal ion doping of ZnS is one of the hottest research topics; e.g., manganese (Mn) doping yields an orange-red color at $\sim 590$ nm and copper (Cu)-doped zinc sulfide is used in electroluminescent (EL) panels.\textsuperscript{45} ZnS:Mn is one of the best candidates for an alternating current thin-film electroluminescent (ACTFEL) device, which is a thin-film stack, typically consisting of a phosphor layer doped with a luminescent impurity (e.g., ZnS:Mn, SrS:Cu, etc.). The film is sandwiched between two insulators that are in turn contacted by an opaque and a transparent electrode.\textsuperscript{47} Some new applications, including nonlinear optical devices, light-emitting diodes (LEDs; when doped), flat panel displays, infrared windows, field emitters, sensors, and lasers have subsequently been discovered.\textsuperscript{48–56}

It is evident that the research on 1D ZnO nanostructures has rapidly expanded in recent years. As pointed out by Zhong Lin Wang in one of the latest reviews, 1D ZnO has been one of the few dominant nanomaterials in nanotechnology together with carbon nanotubes and silicon nanowires.\textsuperscript{54} The number of publications and the cross-referenced areas based on ZnO nanostructures are as large as those for quantum computing, carbon nanotubes, semiconductor thin films, and dark matters.\textsuperscript{54} This comment is also verified by the data in Figure 1, which shows that the number of published papers related to nano-ZnO has rapidly expanded since the early 2000s. ZnS has the closest fundamental physical properties with ZnO. Thus, the interesting nanoscale morphologies and novel properties of ZnS could rival those of ZnO. In fact, the research on 1D ZnS nanostructures has recently become of growing interest due to their potential merit for understanding fundamental physical concepts and for nanoscale optoelectronic devices (Figure 1).\textsuperscript{57–60}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{A plot illustrating the number of published papers related to nano*-ZnO or ZnS each year since the early 2000s. (From Web of Science; the total for 2009 is extrapolated from the data up to June 2009.).}
\end{figure}

1.3. UV Light Emissions, Lasers, and Sensors

UV light, including vacuum UV (VUV)—i.e., UV radiation that is absorbed by air—is electromagnetic radiation with a wavelength shorter than that of visible radiation but still longer than X-rays. It is so named because its spectrum consists of electromagnetic waves with frequencies higher than those that humans identify as the violet color. The irradiation has wavelengths in the range 10–400 nm or energies from 3 to 124 eV.\textsuperscript{45} The UV radiations emitted from the sun are in the range 200–400 nm.\textsuperscript{45}
According to existing classification of UV light with respect to its wavelengths, the longest wavelength of the UV-A band (∼320–400 nm) can reach the Earth’s surface. The molecules in sunscreens absorb most of the UV-B (∼290–320 nm) light and decently protect the human skin, just as the molecules of the Earth’s atmosphere completely absorb the UV-C (∼200–290 nm) radiation and do not allow it to reach the ground—98.7% of the UV radiation that reaches the Earth’s surface is UV-A. Much research has evidenced that UV-A light may cause a skin cancer. Ordinary glass is partially transparent to UV-A but opaque to shorter wavelengths, and silica or quartz glass, depending on quality, can be transparent even to UV wavelengths in vacuum. Ordinary window glass passes ∼90% of the light above 350 nm but blocks over 90% of the light below 300 nm. UV sensors measure the power or intensity of incident UV radiation. Therefore, it is important and demanding to develop novel effective UV sensors that exhibit the highest UV-A sensitivity but are blind to a standard visible radiation.

A laser is a device that emits light (electromagnetic radiation) through a process called stimulated emission. The term laser is an acronym for light amplification by stimulated emission of radiation. Lasers are employed over a huge range of applications, including basic scientific research, tests and measurements, military, industrial processing, information technology, law enforcement, microelectronics, biomedicine, environmental science, avionics, entertainment, telecommunications, and so on. Short-wavelength UV light lasers are particularly desirable for many industrial processes because the light in the UV range permits various types of nonthermal (cold) processing. For example, these processes range from the removal of submicrometer-thick layers of a material (excimer laser eye surgery) to marking an object by UV photon–induced color changes at the surface and/or writing Bragg gratings onto optical fibers.

The research on optical properties of 1D ZnO and ZnS nanostructures has rapidly expanded in recent years and visible emissions centered mainly at 400–650 nm and the band-edge emissions (UV region, ∼368–390 nm for ZnO, ∼330–345 nm for ZnS, as listed in Table 1) at RT or low temperature (LT) have been documented. The possible reason behind the variations in the positions of band-edge emissions in ZnO nanostructures (of different sizes) is the concentration of native defects. In order to achieve an efficient excitonic laser action at RT, the binding energy of the exciton must be much larger than the thermal energy at RT, 26 meV. In this regard, both ZnO and ZnS are good candidates because their exciton binding energies are 60 and 39 meV, respectively, substantially larger than those of ZnSe (22 meV) and GaN (25 meV).

In this review, we will focus on 1D ZnO and ZnS nanostructures in the fields of UV light emissions, lasers, and sensors. We will expand the existing knowledge base and present the most recent examples showing progress in these brand-new fields. In the next sections, we will provide a comprehensive review of the state-of-the-art research activities in ZnO and ZnS nanostructures: UV light emissions, lasers, and sensors. Specific progress with ZnS/ZnO composite nanostructures (including core/shell and heterostructures) and their novel optical properties and potential applications will be also discussed. Other important semiconductor nanostructures (GaN, TiO2, etc.) in the field of UV light emissions, lasers, and sensors will be mentioned. Finally, we conclude this review with certain perspectives and outlook on the future developments in this area.

2. ZnO NANOSTRUCTURES

Since the pioneering works on ZnO nanowire arrays by Zhang et al., ZnO nanobelts by Wang et al., and UV lasers in ZnO nanowire arrays by Yang et al., the synthesis of 1D ZnO nanostructures has been quickly developed. In this section, we will introduce three pioneering studies on 1D ZnO nanostructures and then report systematic and detailed investigations on UV lasers and sensors based on them.

2.1. Three Pioneering Studies on 1D ZnO Nanostructures

2.1.1. ZnO Nanowire Arrays in AAM

The pioneering work on 1D ZnO nanostructures is the fabrication of ordered nanowire arrays and the measurements of their photoluminescence (PL) properties by Zhang et al. The structures were synthesized by oxidizing the Zn nanowire arrays electrodeposited in the nanochannels of anodic alumina membranes (AAM) in air at 300°C for 35 h. The AAM were fabricated by a two-step anodization process, as described in Li et al. and Masuda and Satoh. Optical microscope measurements show that the thickness of the fabricated AAM is ∼50 μm. The transmission electron microscope (TEM, JEM-200 CX) top-view image of the AAM (in Figure 2a) shows an almost perfect hexagonally arranged nanochannel array with a channel diameter of ∼40 nm and an interpore distance of ∼80 nm. Further investigations revealed that the diameters of nanochannels ranged from 15 to 90 nm depending on the types of acid solutions and anodic oxidation parameters. A layer of Au was sputtered onto one side of a membrane (working electrode) in a standard three-electrode electrochemical cell. The electrolyte contained 80 g/L ZnSO4·7H2O and 20 g/L H3BO3. The electrodeposition was performed at 1.25 V with respect to the Ag+/AgCl reference electrode, and carbonate served as the counter electrode at RT. After electrodeposition, the Zn nanowire arrays embedded in AAM were heated in air at 300°C for different periods of time (from 0 to 35 h). X-ray diffraction (XRD) patterns (Figure 3) were taken from nanowire arrays with different heat treatment conditions. No peaks associated with ZnO were found when the pattern was taken immediately after Zn was electrodeposited into the nanochannels of AAM (Figure 3a). Even after being exposed to air at RT for one week, there were no ZnO peaks in the XRD patterns. However, with an increase of heat treatment time at 300°C, the intensities of the Zn peaks became weaker and those of ZnO peaks became stronger (Figures 3b–3d). After heat treatment for 35 h, all Zn peaks disappeared...
FIG. 2. (A) A top-view TEM image of the as-prepared AAM. Two steps of anodization to obtain the AAM were conducted in 0.3 M oxalic acid using 40 V at 14°C. (B) A TEM image of ZnO nanowire arrays embedded in AAM with channel diameters of 40 nm. Reproduced from Li et al.64 Copyright © 2000, American Institute of Physics.

(Figure 3e), indicating that Zn deposited in the channels of AAM had been oxidized completely. In addition, the peak positions and their relative intensities (Figure 3e) are consistent with the standard powder diffraction patterns of ZnO, indicating that there is no preferred orientation and that the ZnO nanowires are polycrystalline. The broadening of ZnO peaks is due to the small particle size. Figure 2b shows a TEM image of AAM with ZnO nanowires in its channels. Compared with the blank AAM, the dark and bright areas correspond to the ZnO nanowires and Al2O3 supporting frame, respectively. The ZnO nanowires with diameters equal to those of the nanochannels are distributed in AAM periodically with a constant interval and form a parallel-aligned array.66 PL measurements showed a blue PL band in the wavelength range of 450–650 nm when 410 nm and a 430 nm excitation wavelength and filter were used, respectively. The PL patterns for an AAM with ZnO nanowires in its channels and blank AAM are shown in Figure 4. The channel diameter of the AAM used here is 20 nm. The PL spectra (Figures 4a–4c) assemblies consist of a strong green emission band peaking around 515 nm. The luminescence intensity decreases with the increase of heat treatment temperature. The luminescence intensity of the blank AAM is much weaker (Figure 4d). Therefore, it can be deduced that the strong green emission band arises from the ZnO nanowire arrays in AAM. Due to the existence of singly ionized oxygen vacancies and the polycrystalline structure of ZnO nanowire arrays, near-band-edge (NBE) emission could not be observed.64

An impressive advantage of ZnO nanostructure usage is the striking ease with which they can be obtained. For example, a recent report from Rao's group demonstrated that merely mixing Zn powder with water at RT for 72 h converts the entire precursor powder to ZnO nanorods having a diameter of \( \sim 50 \) nm (Figure 5).67 Zinc metal on reaction with water slowly gives out hydrogen. The oxygen so liberated reacts with Zn metal to give the oxide nanorods in accord with the following reaction:

\[
Zn(s) + H_2O(l) \rightarrow ZnO(s) + H_2(g)
\]
FIG. 4. PL spectra of ZnO nanowire arrays embedded in AAM (a)–(c) and blank AAM (d). (a) As-prepared and heated at (b) 700°C for 10 h; (c) 900°C for 10 h; (d) 300°C for 35 h. Reproduced from Li et al.64 Copyright © 2000, American Institute of Physics.

Here (s), (l), and (g) represent solid, liquid, and gas phases, respectively. Zn(OH)2 is proposed to be an intermediate herein, whose relatively fast transformation to ZnO at RT is peculiar and needs further investigation. It should be noted that products of similar nature have been regularly reported using more complicated methods. This synthesis is important for incorporation of nanostructures into flexible plastic electronic devices, whose performance and viability is influenced by exposure to high temperature, reactive chemicals, and fabrication-related cost factors.

2.1.2. ZnO Nanobelts

The second pioneering work on 1D ZnO nanostructures is the discovery of ZnO nanobelts, first reported by the Wang’s group in 2001.29 These have well-defined chemical composition, crystallographic structure, and enclosing surfaces.29 Besides ZnO nanobelts, a series of nanobelts of semiconducting oxides have been synthesized by thermal evaporation of oxide powders or mixtures under controlled conditions without the presence of catalyst.68–72 Figure 6 shows a detailed structural characterization of ZnO nanobelts, displaying morphologies that are distinctly different from the nanotubes, nanowires, and nanorods. Each nanobelt has a uniform width in the range of 50–300 nm along its entire length. A cross-sectional TEM image taken from a nanobelt exhibits a rectangle-like cross section (Figure 6d). The typical thickness and width-to-thickness ratios of the ZnO nanobelts are in the range of 10–30 nm and ~5–10, respectively. High-magnification TEM (HRTEM) and electron diffraction (ED) show that the ZnO nanobelts are structurally uniform and single crystalline. Only a few stacking faults are observed that are parallel to the axis and run throughout the entire length of the nanobelt (Figures 6e and 6g).29

2.1.3. UV Lasing in ZnO Nanowire Arrays

The third important study on 1D ZnO nanostructures is the RT UV lasing in ZnO nanowire arrays, as demonstrated by Yang et al.63 The self-organized, ⟨0001⟩-oriented ZnO nanowires...
grown on sapphire substrates were synthesized via a simple vapor transport and condensation process. Using Au thin film as a catalyst for the growth, the authors epitaxially grew the nanowires, which were well oriented on the substrate. Selective nanowire growth could be readily achieved by patterning the Au thin film before the growth. Typical scanning electron microscopy (SEM) images of nanowire arrays grown on sapphire (110) substrates with patterned Au thin films (Figure 7) confirm that the ZnO nanowires grow only in the Au-coated areas. Because of the good epitaxial interface between the (0001) plane of the ZnO nanowire and the (110) plane of the substrate, nearly all of the nanowires grow vertically from the substrates (Figure 7). PL spectra of nanowires were measured with an He-Cd laser (325 nm) as an excitation source. Strong NBE emission at ∼377 nm was observed. Figure 8 shows the RT PL spectra of nanowires with average diameters of 100, 50, and 25 nm. In order to explore the possible stimulated emission from these oriented nanowires, the power-dependent emission was examined by the same authors. The samples were optically pumped by the fourth harmonic of an Nd:yttrium-aluminum-garnet laser (266 nm, 3-ns pulse width) at RT. The ZnO nanowires form natural laser cavities with diameters varying from 20 to 150 nm and lengths up to 10 μm. Under optical excitation, surface-emitting lasing action was observed at 385 nm, with an emission line width less than 0.3 nm (Figure 9). At a low excitation intensity, the spectrum consists of a single broad spontaneous emission peak (Figure 9a) with a full width at half maximum of ∼17 nm. This spontaneous emission is 140 meV below the bandgap (3.37 eV) and is ascribed to the recombination of excitons through an exciton-exciton collision process, where one of the excitons radiatively recombines to generate a photon. As the pump power increases, the emission peak narrows because of the preferential amplification of frequencies close to the maximum of the gain spectrum. Emergence of such sharp peaks in the emission spectra was observed when the excitation intensity exceeded a threshold value (∼40 kW/cm²). Above the threshold, the integrated emission intensity increased rapidly with the pump power (Figure 9b). These short-wavelength nanowire nanolasers can work at RT and the area density of these nanolasers readily reaches 1.1 × 10¹⁰ cm⁻². The chemical flexibility and the one-dimensionality of the nanowires make them ideal for miniaturized laser light sources.
Highlighted by the above-mentioned studies, 1D ZnO has become one of the few dominant nanomaterials for nanotechnology along with carbon nanotubes and silicon nanowires. Most works on 1D ZnO nanostructures have mainly been focused on the rational synthesis, structure analysis, novel properties, and unique applications of ZnO nanorods, nanowires, nanotubes, and nanobelts. The exploitation of UV lasers and sensors is one of the hottest research areas. We will include only representative results in the following subsection due to space limitations.

2.2. Nanolasers Based on 1D ZnO Nanostructures

Figure 10 shows self-organization of a comb structure made of ordered arrays of ZnO nanowires that are monolithically single crystalline. A UV laser array was demonstrated for these comb structures under optical excitation. These nanowire arrays offer an excellent model system to study possible nanolaser interference, coupling, and other nonlinear collective effects. Emission from individual nanowires has been successfully resolved, as seen from Figure 10. Each bright emission spot in Figure 10b corresponds to a single tip of the nanowire array. Figure 10c shows power-dependent PL spectra recorded on the comb structure. The authors also demonstrated that ZnO nanobelts with pseudo-dependent cross sections can be excellent microcavities with a high quality factor of ∼3,000, and it was further found that the lasing threshold had inversely been proportional to the length of the belt before the pumping intensity reached the saturation region. In 2004, Cao et al. observed UV-stimulated emissions and “whispering gallery mode” phenomena within ZnO nanowires that were prepared through a simple reduction reaction method in a tube furnace, using an excitation of the 325-nm line of an He-Cd laser of ∼100 W/cm². Recently, the synthesis and optical characterization of individual ZnO vertical nanocavities were presented by Yang et al. Dilute arrays of ZnO vertical nanowires with interwire distances of 2–50 µm were grown by a modified Chemical Vapor Transport (CVT) method. A new method based on three-dimensional (3D) mapping of the PL emission of single vertical nanowires was utilized using UV-laser scanning confocal microscopy. This unique method of high-resolution microscopy...
FIG. 9. (a) Emission spectra from nanowire arrays below (line a) and above (line b and inset) the lasing threshold. (b) Integrated emission intensity from nanowires as a function of optical pumping energy intensity. (c) Schematic illustration of a nanowire as a resonance cavity with two naturally faceted hexagonal end faces acting as reflecting mirrors. Reproduced from Huang et al. Copyright © 2001, American Association for the Advancement of Science.

Combines a UV laser focused to a diffraction-limited spot (∼220 nm) with digital scanning electronics and a UV-enhanced detection system to image the PL emission from planar sections of a ZnO vertical nanowire from its base to tip. Stimulated emission in vertical nanowire cavities was generated by 266-nm excitation pulses from the fourth-harmonic of an Nd:YAG laser focused onto the sample at a grazing angle of 16 degrees with respect to the substrate plane. A 3D mapping of the PL emission intensity and lasing spectra from a single vertical nanowire are displayed in Figure 11. The vertical feature is a representation of the band-edge PL emitted from an individual nanowire at a given focal plane. The lasing threshold was measured to be 400 μJ/cm². As also shown in Figure 11, the spatial selectivity of confocal microscopy was also utilized to image the PL emission in vertical sections of a nanowire. This was performed by raising or lowering the focal plane of the diffraction-limited spot with respect to the sample during successive scans on an individual nanowire. This unique characterization method could provide highly selective optical characterization of hetero/nanostructures emerging in the field of optoelectronics and nanophotonics, which is unattainable by conventional microscopy.

2.3. Optical Properties of ZnO Nanostructures

Optical properties of a variety of forms of ZnO, including 1D ZnO nanostructures, have been studied by PL and cathodoluminescence (CL) spectroscopies. Compared to other techniques, such as PL, CL has the advantage of much higher spatial resolution, up to few nanometers. It is one of the most widely used techniques to investigate local optical properties of materials. Moreover, by using electron beams with different energies, it is possible to probe the optical behavior of a material at different depths from the surface. Two examples on tuning PL properties of Sn-doped ZnO nanobelts by altering flowing atmosphere and CL properties of pure and N-doped ZnO nanobullets are highlighted below.

2.3.1. Tuning PL Properties of Sn-Doped ZnO Nanobelts

The synthesis of Sn-doped ZnO nanobelts was carried out using a tube furnace. High-purity (99.99%) zinc powders were placed in a ceramic boat that was inserted at the center of the horizontal tube furnace. A tin-coated Si wafer was placed downstream in the tube. The system was rapidly heated to 700°C and kept at this temperature for 30 min in different flowing atmospheres (air [no flow], dry and humid argon [Ar] flow, and argon/oxygen [O₂] gas mixture, flow rate of 100 sccm [standard cubic centimeter per minute]). Water was inserted into the reaction by placing a water-filled alumina crucible in the upstream side of the alumina tube for humid Ar flow, and the ratio of the gases Ar/O₂ was 5:1.

The structure and morphologies of the products synthesized under different flowing atmosphere were almost the same. Here,
FIG. 10. A dendritic nanowire UV laser array. (A) SEM image of comb structures of ZnO nanowires. (B) Far-field optical image of spatially resolved light emission from individual nanowires displaying comb structures. The spacing between the wires is ca. 1 µm. (C) Power-dependent emission spectra from the comb structure. From bottom up, the excitation energy densities are 252, 505, 580, 707, and 883 nJ/cm², respectively. Reproduced from Yan et al. Copyright © 2003, American Chemical Society.

FIG. 11. (A) 3D-rendered confocal scanned PL image of a ZnO vertical nanowire cavity. (B) SEM image of an individual ZnO vertical nanowire. (C) Diagram of the ZnO vertical nanowire cavity with corresponding PL images. (D) Lasing spectra of the single ZnO vertical nanowire cavity. Reproduced from Gargas et al. Copyright 2009, American Chemical Society.
we discuss the products synthesized under Ar flow as a general representation. Figure 12a shows an XRD pattern of the as-synthesized samples that were obtained under the Ar flow. There are no diffraction peaks originated from Sn and its compounds, and all the peaks can be indexed to a hexagonal wurtzite-structured ZnO. This indicates that the impurities do not change the wurtzite structure of ZnO. SEM investigation shows that the nanobelts prepared under different flowing atmospheres have almost uniform widths of $\sim 800$–1,500 nm, thicknesses of $\sim 20$–60 nm, and lengths that range from several tens of micrometers to the order of millimeters. Figure 12b is a low-magnification SEM image of the synthesized Sn-doped ZnO nanobelts obtained under the Ar flow. It shows numerous Sn-doped ZnO nanobelts. Figures 12c and 12d are the high-magnification SEM images of an individual Sn-doped ZnO nanobelt. They reveal that the nanobelt has a width of $\sim 800$–1,500 nm, a thickness of $\sim 20$–60 nm, and a length in the range of several tens of micrometers.

Further structural characterizations were carried out using TEM. Figure 13a shows an individual Sn-doped ZnO nanobelt with a width of $\sim 1,400$ nm. The width is uniform along the entire structure length. High-resolution TEM and the corresponding fast Fourier transform (FFT) patterns provide further insight into the belt microstructures. As shown in Figure 13d (HRTEM image and its FFT [inset]), the nanobelt (Figure 13a) has a hexagonal wurtzite structure and grows along the [2-1-10] direction with its top/bottom surface being $\pm (0001)$. The side surfaces are $\pm (01-10)$ (inset in Figure 13a). Most of the Sn-doped ZnO thin and wide nanobelts are single crystalline without dislocations and defects (Figure 13d), and their geometrical shapes are uniform. The surfaces are clean and flat. However, planar defects are observed occasionally, whereas dislocations are rarely seen. Figure 13b shows the TEM image and the corresponding HRTEM image (inset) of an individual Sn-doped ZnO nanobelt with a uniform distribution of planar defects along its entire length. Energy-dispersive X-ray spectroscopy (EDX) identifies that the structures consist of Zn, O, and Sn (Figure 13c). The Sn content is $\sim 5$ at.%. The Cu peaks come from the TEM grid.

Figure 14a displays the room-temperature PL spectra of the Sn-doped ZnO thin and wide nanobelts prepared under different flowing atmospheres. The excitation wavelength was 325 nm. An NBE peak at 370 nm and a green emission band centered at 518 nm were observed for Sn-doped ZnO thin and wide nanobelts. The NBE emission peak showed a blue shift ($\sim 0.024$ eV) compared to a bulk ZnO single crystal. Thus, the doping of Sn in ZnO nanobelts can adjust the band emission. The blue shift of NBE emission is due to the Burstein-Moss effect with an increase in bandgap value governed by Sn doping. ZnO is naturally an n-type material with the Fermi level inside the conduction band (by the quantity $\xi_n$ when it is heavily doped). Because the states below $\xi_n$ of the conduction band are filled, the absorption edge should shift to the higher energy by $\xi_n$ and the NBE emission has a blue shift. The green emission band
FIG. 13. Structures of the Sn-doped ZnO thin and wide nanobelts. (A) and (B) A low-magnification TEM image and the corresponding HRTEM image and its FFT recorded from a typical unselected Sn-doped ZnO nanobelt, showing single-crystal, dislocation-free volume. The inset in (A) is the structure model of the Sn-doped ZnO nanobelts. (B) A uniform distribution of planar defects along the entire nanobelt is observed occasionally and the inset in (B) is the corresponding HRTEM image. (C) EDX data show 5 at.% Sn. (D) Most of the nanobelts are single crystalline without dislocations and defects. Reproduced from Fang et al.101 Copyright © 2005, The Chemical Society of Japan.

at 518 nm originates from the recombination of the holes with electrons occupying the singly ionized O vacancies. The intensity ratio of the NBE to the green emission is determined by the concentration of O vacancies in the nanobelts; therefore, it has become possible to selectively enhance the NBE emission performance by altering the synthesis parameters, such as the flowing atmosphere in the furnace. A higher reaction activity and/or higher partial pressure of oxygen will decrease the concentration of O vacancies in the structures. It can be observed from Figure 14b that the ratio of the NBE to green emission is dramatically enhanced when the reaction activity of oxygen in the furnace is increased with the flowing atmosphere changing from dry Ar, to air (no flow), to humid Ar, and to Ar/O₂ gas mixture.66,101

2.3.2. CL Properties of Pure and N-Doped ZnO Nanobullets

One of the most interesting morphologies of ZnO nanostructures is nanobullets, 1D-like single crystals having a sharp tip and a flat base.100 These were synthesized by a simple
hydrothermal technique and are the consequence of unusual crystal growth, where a reaction intermediate permits growth of the crystal only in one direction, leading to these unusual structures. The optimal conditions to obtain ZnO nanobullets require a large excess of ethanol (Zn/ethanol concentration of ca. 1:500). The preparation conditions induce a unilateral growth from base to tip of nanobullet-like structures, despite the absence of any template. This same procedure was further extended for the synthesis of N-doped ZnO nanobullets, which is the first solution-based approach for N-doped ZnO.100

The reaction of zinc nitride with water to form ammonia and zinc oxide is well known, \[ \text{Zn}_3\text{N}_2 + 3\text{H}_2\text{O} = 3\text{ZnO} + 2\text{NH}_3. \] This is a vigorous exothermic reaction at RT. Nitrogen doping can be achieved by pursuing the reverse reaction under hydrothermal conditions and in the presence of large excess of ammonia. Details of experimental processes and structural characterizations can be found in Gautam et al.100 Investigations of the CL properties on individual nanobullets revealed that the N doping might not be uniform within a single structure, but the core is N-rich, whereas the surface is N-poor. N doping causes a significant 0.024-eV red shift of the CL emission peak.

Figure 15a is a typical CL spectrum acquired from a pure ZnO nanobullet at RT. The spectrum consists of a narrow and strong UV peak centered at 381 nm (\(~3.2 \text{ eV}\)) and broad, low-intensity luminescence in the visible region. The authors observed that the UV peak position varied from 380 to 385 nm, whereas the visible luminescence is absent in many nanobullets. Figures 15b and 15c show a typical SEM image of a pure ZnO nanobullet and its corresponding CL image. The latter reveals uniform luminescence that arises entirely from the nanostructure alone.100

For investigating local optical properties of a ZnO nanobullet (SEM image in Figure 16a), a number of CL spectra, acquired at various locations along the line shown in this image, are plotted in Figure 16b. The spectra are relatively uniform, whereas the intensity of the UV peak gradually changes along the nanostructure. The intensity is low near the bullet tip and increases with diameter of the nanobullet. The UV peak observed in this study can be ascribed to the NBE emission, and the visible peak is ascribed to the deep-level emissions (DE: 550 nm). Figure 16c shows the CL spectra acquired at different voltages. The intensity was found to increase as the applied voltage changed from 5 to 19 kV. However, the peak position has only a marginal red shift from 385 to 389 nm. This implies that the optical transitions near the surface and the core of the structure are nearly identical.

The CL properties of the N-doped ZnO samples have distinctly different features from those of the pure ones. As observed in Figure 17, the CL spectra for the pure and doped samples are nearly identical at 5 kV, whereas there is a red shift of the NBE peak position of a N-doped sample by \(~30 \text{ nm} \) (0.024 eV) as the voltage is increased to 15 kV. In addition, the relative intensity of the DE peak increases. The main differences in optical properties between a pure and an N-doped ZnO nanobULLET are summarized in Figure 17c. CL spectra were acquired from 15 equally spaced spots (beginning from the tip) along each nanobullet at 5 kV to probe near the surface regions and at 15 kV to probe the core. Figure 17c depicts the plot of the NBE peak positions observed along the nanobullets. This indicates that the variations of the NBE peaks within a pure nanobullet are minimal (standard deviations \(< 2\)). Similar uniformity with a slight red shift was also observed near the surface (at 5 kV) for the N-doped sample. On the other hand, a 15-kV electron beam gives larger shifts and variations (standard deviations \(> 3.9\)) in the NBE peak positions, indicating that the doped N content at the exterior of the ZnO nanobullets is lower and more uniform than at the core (schematic in the inset of Figure 17c). It is suggested that the limited supply of ammonia affects the nitrogen incorporation and maximum doping takes place at the early stages of growth. Another factor is the high energy; i.e., the electron beam induces N desorption near the surface.100
2.4. ZnO Nanostructures as UV Light Sensors

Equally important to light generation in nanoscale structures is the need to efficiently detect optical inputs and process them as electrical outputs. For example, for photodetection, a nanowire is configured to monitor the photocurrent as a function of photon excitation. In such schemes, a constant bias across the nanowire is applied, and instead of using a gate to induce current fluctuations, an optical flux forces the wire to change from an insulating to a conducting state. This type of layout is termed linear nanowire photodetector because the photocurrent is proportional to the number of carriers produced within the semiconductor by an optical absorption process.\(^{102}\) Because of the high

SVR, trapping at surface states drastically affects the transport and photoconduction properties of 1D nanostructures, and so wide-bandgap ZnO has been widely used for nanometer-scale visible-light-blind UV-light sensors or photodetectors with high sensitivity and selectivity.
FIG. 18. A schematic of the photoconduction mechanism generated on a ZnO nanowire photodetector. (a) Schematic of a nanowire photoconductor. (b) and (c) Trapping and photoconduction mechanism in ZnO nanowires. Reproduced from Soci et al. Copyright © 2007, American Chemical Society.

2.4.1. Photoconduction Mechanism of ZnO Nanowire Photodetector

Figure 18 shows a schematic of the photoconduction mechanism in the presence of a high density of hole-trap states at the ZnO nanowire surface. When illuminating under the photon energy larger than the semiconductor bandgap (\( h\nu > E_g \)), electron-hole pairs are photogenerated (\( h\nu \rightarrow e^- + h^+ \)) and holes migrate to the surface along the potential slope created by the band bending, leaving behind unpaired electrons, which increase the conductivity under an applied electric field (Figure 18a). Figure 18b illustrates the trapping and photoconduction mechanism in ZnO nanowires, and the top inset shows the schematic of the energy band diagrams of a nanowire in the dark, indicating band-bending and surface trap states. VB and CB are the valence and conduction bands, respectively. The bottom drawing shows oxygen molecules adsorbed at the nanowire surface that capture the free electron present in the n-type semiconductor forming a low-conductivity depletion layer near the surface [\( O_2(g) + e^- \rightarrow O_2(ad) \)]. Under UV illumination, photogenerated holes migrate to the surface and are trapped [\( O_2(ad) + h^+ \rightarrow O_2(g) \)], leaving behind unpaired electrons in the nanowire that contribute to the photocurrent (Figure 18c).

2.4.2. Individual ZnO Nanowire Photodetector

The first individual ZnO nanowire-based UV photodetectors and optical switches were reported by Yang et al. in 2002. The ZnO nanowires used in the experiments were grown by a vapor-phase transport process. The diameters of these wires ranged from 50 to 300 nm. To characterize their photoconducting properties, the nanowires were dispersed directly on prefabricated gold electrodes (Figure 19a, inset). Alternatively, electron-beam lithography was used to fabricate gold electrodes on the top of the nanowires. The nanowires were insulating (resistivity of >3.5 MΩ·cm) in the dark state and became conductive under UV exposure, with up to a million times lower resistivity under illumination. Figure 19a shows the current-voltage (I-V) characteristics of an ZnO nanowire (diameter ~60 nm) dispersed on four terminals in the dark and under illumination from a handheld UV lamp (0.3 mW/cm² at 365 nm). A larger photoresponse was detected at a higher bias. It is noted that the I-V curve for the UV-exposed nanowire exhibits nonlinear behavior. The measurements were carried out using a Keithley source-measure unit at RT. The large increase in current was observed only when resonant excitation wavelengths shorter than the bandgap (~370 nm) illuminated the wire. This implies that the ZnO detector is an excellent optical switch (Figures 19b and 19c). The photoresponse is strongly dependent on the ambient gas conditions, being slow in vacuum and inert gases (up to several minutes) and fast in air (<1 s), indicating the role of ambient oxygen.

2.4.3. Facile Routes to Enhance UV Light Response of ZnO Nanostructures

Following the above-mentioned facts, great progress in enhancing the sensitivity to UV light response based on ZnO nanostructures has been achieved. For example, a UV photodetector fabricated using a single ZnO nanobelt has shown a photoresponse enhancement up to 750 times compared to a bare ZnO nanobelt after coating with a ~20-nm plasma-polymerized acrylonitrile nanoscale film. This effect is suggested to be a consequence of the high efficiency of exciton dissociation under UV illumination and may be due to efficient electron transfer from the valence band of a ZnO nanobelt to the acrylonitrile and then back to the conduction band of ZnO. In a similar way, Lao et al. demonstrated that the UV response of
a ZnO nanobelt-based sensor had been enhanced nearly 5 orders of magnitude after functionalizing its surface with a polymer with a high UV absorption ability. This giant enhancement in photoconductance was attributed to the energy levels introduced by the polymer lying in the corresponding band gap and in the conduction band of ZnO. Such states served as “hopping” states and increased the excitation probability of an electron to the conduction band. The details of the device fabrication are described in Lao et al. The photoconductance response of the single ZnO nanobelt devices functionalized with different polymers is shown in Figure 20a. The data are plotted for the ratio of the conductance measured when the UV was on (G) and off (G₀). The UV source used in the experiment had a wavelength distribution around 280 nm. The results imply that the conductance of uncoated ZnO nanobelt devices increased by 2.8 times upon UV illumination, ~50 times for a polystyrene-co-maleic acid (PS-co-MAc)-coated ZnO nanobelt, and 100 and 15 times for poly N-isopropylacrylaamide (PNIPAM) and carboxymethylcellulose (CMC)-coated ZnO nanobelts, respectively. However, by using a polystyrene sulfate (PSS)-coated ZnO nanobelt, photoconductance increased by 75,000 times when UV was on. Figure 20b displays the UV absorption spectra of the four polymers used in this study. PS-co-MAc MA, PNIPAM, and CMC, show a UV absorption peak at wavelengths around 190–200 nm and very weak absorption at the 280-nm wavelength. In contrast, there are two absorption peaks around 190 and 260 nm for the UV absorption spectrum of PSS. These match well the excitation wavelength of the UV source. The data suggest that the large absorbance of the PSS to the UV is likely responsible for the observed huge increase in photoconductance. Lao et al. proposed that the absorption peak around 260 nm and the related molecular energy states in PSS play a significant role in enhancing the photon response. Figures 20c and 20d present a schematic illustration of the electron-hole generation process with facilitation of transition states from the molecular energy states in PSS and photon-induced carrier transportation process in a ZnO NB by UV light illumination. The role played by PSS is to serve as a hopping-state or bridge for the electron transfer.

3. ZnS Nanostructures

3.1. Optical Properties of ZnS Nanostructures

Although much research has been devoted to the optical properties, such as CL and PL, of 1D ZnS nanostructures, very few studies have been reported on their possible UV bandgap emission at RT. This is mainly due to high sensitivity of the 1D ZnS nanostructure optical properties to the synthetic conditions, its crystal size and shape, and intrinsic defects such as vacancies and interstitials, etc.

3.1.1. Visible Emissions of ZnS Nanostructures

As the literature documents, for a large number of 1D ZnS nanostructures of various shapes synthesized using different
FIG. 20. Giant enhancement in UV response of ZnO nanobelts by polymer surface functionalization. (a) Normalized conductance responses of individual ZnO nanobelt devices of bare nanobelt and surface functionalization with different polymers upon UV illumination being turned on and off. (b) UV absorption spectra of surface functionalization ZnO nanobelts with different polymers. (c) and (d) Possible mechanism on electron-hole generation process for PSS-coated nanobelt devices. Reproduced from Lao et al.104 Copyright © 2007, American Chemical Society.

methods, in general, there are two and more visible characteristic optical peaks.105–108 For example, Wang and Zhang et al. reported the synthesis of single-crystalline high-purity ZnS nanowires via a simple and low-cost thermal evaporation method in the presence of an Au catalyst.105 ZnS nanowires have diameters of ~30–60 nm and lengths up to several tens of micrometers. After examining the RT PL of the ZnS nanowires, as shown in Figure 21a, two emission bands have been detected in the PL spectra, at ~450 and ~520 nm. The authors attributed these emission peaks to the surface states of ZnS nanowires and the presence of Au ions.105 ZnS nanobelts with a width from 40 to 120 nm, a thickness of ~20 nm, and a length of several micrometers were synthesized by a simple thermal evaporation method in an N₂ atmosphere containing a small amount of CO and H₂ gases. A weak emission band at 450 nm and a strong emission band around 600 nm were observed in PL emission, as shown in Figure 21b. They were assigned to defect-related emission of the ZnS host and the emission from traces of Mn²⁺.

FIG. 21. (a) RT PL spectrum of ZnS nanowires synthesized via a simple and low-cost thermal evaporation method with the presence of an Au catalyst. Reproduced from Wang et al.105 Copyright © 2002, Elsevier B.V. (b) RT PL spectrum of the ZnS nanobelts fabricated by a simple thermal evaporation method in an N₂ atmosphere containing a small amount of CO and H₂ gases. Reproduced from Zhu et al.106 Copyright © 2003, American Institute of Physics.
impurities, which are incorporated during the synthetic process.\textsuperscript{106} As an alternative method, using hydrazine hydrate (N$_2$H$_4$·H$_2$O) as a solvent, bundles of wurtzite ZnS nanowires with diameters of 10–25 nm and lengths of $\sim$5–8 $\mu$m have been synthesized via a solvothermal route. PL measurements revealed one weak peak at 465 nm and two strong peaks at 413 and 438 nm. The authors suggested that the S vacancies and interstitial S atoms and surface states could be responsible for the strong emission bands at 413 and 438 nm and a weak peak at 465 nm, respectively.\textsuperscript{107}

As an important member of the inorganic nanotubes family (due to their high SVR), the synthesis of ZnS nanotubes has recently been of growing interest.\textsuperscript{108–111} Wang et al. reported the synthesis of ZnS nanocables and nanotubes by a chemical reaction using as-synthesized ZnO nanobelts as a template. These structures were composed of ZnS nanocrystallites of $\sim$7 nm in size and had a high percentage of pores.\textsuperscript{108} Figure 22a displays the typical SEM images of hexagonal-faceted ZnS nanotubes, which were synthesized via a high-temperature thermochemistry process.\textsuperscript{110} The tubes are single crystalline and of a wurtzite-type with hexagonal cross sections. Most of them grow along the [0001] direction and are closed by low-index faces. They are very pure with no coatings and filling impurity phases. As shown in Figure 22a, the tubes usually have a length of several micrometers, a uniform outer diameter of 100–200 nm, and a tube-wall thickness of $\sim$10 nm. The formation of these nanotubes is a self-assisted growth process because no templates or metal catalysts have been adopted.\textsuperscript{110} Figure 22b displays a typical PL spectrum of the nanotubes at RT. The spectrum consists of a weak blue emission centered at 439 nm and a strong green emission centered at $\sim$538 nm. They have been assumed to arise from the large SVR of the nanotubes and the stoichiometric defects including self-activated centers, vacancy states, and interstitial states.\textsuperscript{110} By using metal organic chemical vapor deposition (MOCVD) template methods, wurtzite-phase ZnS nanotubes arrays were synthesized in the pores of the porous AAM by Zhai et al.\textsuperscript{111} Different from conventional thermal evaporation and CVD methods in which a ZnS powder/nanopowder or ZnS-based mixture have always been adopted as source materials, herein low-pressure thermal decomposition of zinc bis(diethylthiocarbamate) [Zn(S$_2$CNEt$_2$)$_2$] has been employed. The well-ordered and polycrystalline ZnS nanotubes with 140–250 nm outer diameter and several tens of micrometers in length were formed. A strong blue-green emission centered at 510 nm was observed.\textsuperscript{111}

Besides familiar 1D ZnS nanostructures, unusual and novel tetrapod-like ZnS nanopods and single-crystalline ZnS nanoawls were successfully synthesized by Zhai and coworkers, and their optical properties were investigated in detail.\textsuperscript{59,112} For example, single-crystalline ZnS nanoawls were achieved at a large scale by a simple two-step pressure-controlled vapor-phase deposition at a relatively low temperature of 800 $^\circ$C using a mixture of commercial ZnS and SnO$_2$ and graphite powders. A molar ratio was 5:1:3 and single-crystalline Si wafers covered with silver were taken as deposition substrates.\textsuperscript{112} As shown in Figure 23a, awl holders were rectangle shaped and faceted, and the diameters of the awl tips were in the range of 100–200 nm. The details for the synthesis, characterization, and growth mechanism can be found in Zhai et al.\textsuperscript{112} An RT PL spectrum of the synthesized ZnS nanoawls is shown in Figure 23b. A stable and strong green emission band centered at 513 nm and a weaker blue emission band centered at 447 nm are seen. Based on their experimental observations and previous studies, Zhai et al. suggested that the blue emission at 447 nm could be ascribed to the transitions involving vacancy states, whereas the observable green emission for ZnS nanoawls had been caused by some self-activated centers, vacancy states, or interstitial states associated with the peculiar nanostructures.\textsuperscript{112} These unique ZnS nanostructures obtained via a simple synthesis strategy guarantee high
FIG. 23. (A) A typical SEM image of the as-synthesized ZnS nanoawls via a simple two-step pressure-controlled vapor-phase deposition. (B) RT PL spectrum of the synthesized ZnS nanoawls using an He-Cd laser with an excitation wavelength of 325 nm. Reproduced from Zhai et al. 112 Copyright © 2007, American Chemical Society.

As one of the pioneering works in the field of controlled growth of nanostructured materials, ZnS nanostructures with different morphologies, sizes, and microstructures were formed by the evaporation of ZnS nanopowders at 1,100 °C for 30 min, with Ar both as a protecting medium and a carrying gas. The structures were obtained in a narrow temperature range between ~850 and 1,050 °C and a long deposition length of ~54 mm using different substrates with/without nanoscale gold films. 113 Figure 24 shows the typical SEM images of four kinds of ZnS nanostructures, including nanorods, nanowires, nanobelts, and nanosheets. 113 All experimental results suggested that the temperature distribution inside the tube furnace and catalyst played the dominant roles in the formation of nanostructures. Within a certain temperature range, products with a specific morphology were obtained. Therefore, it may be possible to obtain ZnS nanostructures with a specific morphology by controlling the reaction temperature and a catalyst. There exist two growth mechanisms for ZnS nanostructures, a VLS mechanism for ZnS nanorods and nanowires and a VS mechanism for ZnS nanobelts.

FIG. 24. Temperature-controlled and catalytic growth of ZnS nanostructures with four kinds of ZnS nanostructures, including (A) nanorods, (B) nanowires, (C) nanobelts, and (D) nanosheets by the evaporation of ZnS nanopowders. Reproduced from Fang et al. 113 Copyright © 2005, Wiley-VCH.

FIG. 25. PL spectra of as-synthesized ZnS nanostructures: (a) nanorods, (b) nanowires, (c) nanobelts, and (d) nanosheets measured with an excitation of the 375-nm line of an Xe lamp at room temperature. Reproduced from Fang et al. 113 Copyright © 2005, Wiley-VCH.
and nanosheets. The details for the controlled growth and the effects of substrate temperature and catalyst on the growth of ZnS nanostructures can be found in Fang et al.\textsuperscript{113} Figure 25 depicts a typical PL emission of the above-mentioned four kinds of ZnS nanostructures.\textsuperscript{113} It can be seen that the ZnS nanorods and nanowires have almost the same PL band positions A. Stable and strong green emission band centered at \( \sim 530 \text{ nm} \) and a weaker blue emission band centered at \( \sim 440 \text{ nm} \) are detected. The ZnS nanobelts and nanosheets have almost the same PL band positions; e.g., a stable and strong green emission band centered at \( \sim 545 \text{ nm} \) and a weaker blue emission band centered at \( \sim 440 \text{ nm} \).\textsuperscript{113}

As an alternative method to study the optical properties of nanostructured materials, CL measurements have been carried out on 1D ZnS and its derivatives. For example, CL and its mapping on a flower-like ZnO, a ZnO/ZnS core-shell, and a tube-like ZnS nanostructure were investigated in detail.\textsuperscript{114} A UV emission at 380 nm and a yellow emission at 600 nm induced by interstitial oxygen were found for flower-like ZnO nanostructures. An enhanced UV emission and weaker defect emission were detected for ZnO/ZnS core-shell nanostructures, and only a weak defect emission was collected from tube-like ZnS nanostructures due to S vacancies.\textsuperscript{114}

### 3.1.2. Origins of Visible Emissions of ZnS Nanostructures

One can obtain the UV bandgap emission at RT only if one learns the origins of visible peaks and then suppresses them on purpose. Through the analysis of numerous experiments, we showed that one of the visible peaks around 535 nm is related to elemental S species on the ZnS nanostructure surfaces under certain specific synthesis conditions.\textsuperscript{115,116} In these experiments, the ZnS nanobelts with a pure wurtzite phase were synthesized by a thermal evaporation method in a H\(_2\)S (20\%)/Ar (80\%) atmosphere at 1,100°C during heating over 2 h with the gas flow rate of 40 sccm. Our conclusion was substantiated by using structural analysis from HRTEM, EDX, X-ray photoelectron spectroscopy (XPS), PL, excitation techniques, etc. For example, XPS analyses showed that the enrichment of sulfur on the surface of ZnS nanobelts is apparent because the atomic ratio of S to Zn is \( \sim 2:1 \). The intensities of the PL peak at 535 nm, as well as the photoluminescence excitation (PLE) peaks, decrease significantly after the UV light (\( \sim 3–4 \text{ eV} \) in this experiment) illumination. The short lifetime within a sub-nanosecond scale makes this PL band very efficient against the self-activated blue band and also precludes the operation of Cu and Al codoped emission.\textsuperscript{115} Moreover, the green band emission shows an anomalous blue shift–red shift transition and the half-width undergoes a narrowing-broadening transition with decreasing temperature. From the integrated PL intensity measurements as a function of temperature, the anomalous temperature-induced emission shift was found to strongly relate to thermal population in localized energy states due to the unsaturated orbitals of dangling bonds in the surface sulfur.\textsuperscript{116}

By combining high-resolution CL measurements and HRTEM observations, the origin of the CL peaks and their relation to the microstructure within the same individual nanostructure was understood. The results indicated that another conventional visible band emission most likely originated from the twin-like defects. To study possible origin of other visible peaks, the experiments are still ongoing.

### 3.1.3. UV Emissions of ZnS Nanostructures

Based on these conclusions and a large number of experiments, we developed an effective road map to control the microstructures and the crystallography in ZnS. At the end, ZnS nanostructures with sharp UV emission (\( \sim 330–340 \text{ nm} \)) at RT were created.\textsuperscript{117–119} Two typical examples of multangular branched ZnS nanostructures with needle-shaped tips exhibiting sharp UV bandgap emission and broad visible emission and single-crystalline ZnS nanobelts with sharp UV emission at RT (assembled as UV sensors) are introduced below.\textsuperscript{118,119}

#### 3.1.3.1. Multangular Branched ZnS Nanostructures with Needle-Shaped Tips

We developed a facile and effective route toward the synthesis of ZnS multangular branched nanostructures with needle-shaped tips, a potential luminescent and field-emitter nanomaterial. The synthesis of these multangular branched ZnS nanostructures was carried out via conventional thermal evaporation in a horizontal tube furnace with a 36-mm inner-diameter quartz tube.\textsuperscript{118} The key message in this work is that the growth of ZnS nanostructures with special morphologies could easily be controlled by gradual reduction of heating temperature from 1,050 to 700°C over 30 min. The detailed
FIG. 27. ZnS multiangular branched nanostructures with needle-shaped tips. (A) XRD pattern recorded from a product. (B) and (C) Different magnification SEM images verifying the multiangular and needle-shaped structures. Reproduced from Fang et al.118 Copyright © 2008, American Chemical Society.

After the synthesis, the products were characterized by XRD, SEM, TEM, EDX, and ED techniques. A typical XRD pattern of a product is shown in Figure 27a, where all the diffraction peaks within an experimental error can be indexed to wurtzite-type ZnS with the lattice constants of $a = 0.382$ nm and $c = 0.626$ nm (Joint Committee for Powder Diffraction Studies [JCPDS] Card: 36-1450). Different magnification SEM images in Figures 27b and 27c show that the ZnS crystals are composed of multiangular branched nanostructures with needle-shaped tips. A diameter of each needle-shaped branch decreases along its length from the center toward the tip. Each arm has a straight appearance with the needle length reaching several micrometers.

Figure 28 displays TEM and HRTEM images, ED pattern, and EDX spectrum of a single arm within a multiangular nanostructure. The length of the arm, shown in Figure 28a, reaches several hundreds of nanometers. HRTEM images of the tip and stem (Figures 28b and 28c) suggest that the surface of the entire branch is clean and atomically sharp. It is free of dislocations or stacking faults. Each arm grew along the same direction; that is, [0001]. The EDS spectrum, shown in Figure 28d and taken from the stem, confirms that it consists of Zn and S with a stoichiometric ZnS composition. The Cu peaks come from a TEM grid. The similar spectra were obtained in various spots on the arms and their tips on numerous nanostructures. Each tip was composed of chemically pure, structurally uniform, single-crystalline, and defect-free ZnS. From TEM and SEM observations of over 100 nanostructures, we found that the multiangular branched ZnS nanostructures have mainly been composed of biangular structures (~20%), triangular structures (~50%), tetraangular structures (~20%), and some multiangular nanostructures (~10%). Besides the above-mentioned multiangular branched ZnS nanostructures, some individual ZnS nanowires with needle-shaped tips or their assemblies were observed. The average width at the sharp tips was ~8 nm. By analyzing the experimental results, we suggest that VS mechanism dominates the growth of the present unusual structures.118

High-spatial-resolution CL from individual ZnS multiangular branched nanostructures was investigated with the nanometer resolution. The size-dependent optical spectra exhibited sharp UV bandgap emission and broad visible emission at RT. Figures 29a and 29b show a typical individual ZnS multiangular branched structure and its CL spectrum obtained at RT. This consists of a sharp UV emission band centered at ~334 nm and a broad visible emission band centered at ~404 nm. The inset in Figure 29b is the enlarged portion of the sharp UV emission band. The intensity ratio between the UV emission and visible emission is ~1/10. Figures 29c and 29d display CL images of the same nanostructure recorded at 334 and 404 nm, respectively. Similar CL spectra, shown in Figure 30, were collected from many other individual ZnS multiangular branched structures. They only reveal slight variations in the peak positions. In order to further study spatial variations of the optical properties, the CL spectra were collected in different spots along the individual tapered arms of varying diameter, as depicted in

experimental parameters are shown schematically in Figure 26. The furnace was heated to 1,050°C in 9 min and then the reaction temperature was decreased to 700°C in 30 min. A constant cooling rate of ~12°C min$^{-1}$ was applied to reduce the temperature to a desired value. Then the system was allowed to cool down to RT naturally.118
Figure 28. (a) TEM image of the individual arm of a multiangular branched nanostructure; (b) and (c) the corresponding HRTEM images of its tip and stem, respectively. The inset in (c) shows the corresponding ED pattern. (d) EDS spectrum taken from the arm, shown in (a). Reproduced from Fang et al. Copyright © 2008, American Chemical Society.

Figure 31. Figures 31a and 31b display an SEM image and the corresponding CL image of the nanostructure. This shows uniform luminescence that entirely arises from the nanostructure alone. The RT CL spectra (Figure 31c), denoted as C1, C2, C3, C6, C9, C12, C15, C16, and C17, were acquired at various spots between the two red lines in Figure 31b. The CL UV emissions are very strong and sharp in some spots. The centers of the UV emissions shifted gradually from 337 to 333 nm (≈0.043-eV blue shift) with diameter descending, whereas the broad visible emissions changed between 398 and 425 nm. The CL UV emission from the samples was stable against a prolonged exposure to air and from one measurement to another. The CL spectra remained unchanged, being consecutively recorded within a period of nearly one year. It is assumed that the CL UV emission centered at ≈333 to 337 nm represents the band-edge luminescence, suggesting the bandgap energy of ≈3.7 eV for the present wurtzite-type ZnS nanostructures.

3.1.3.2. Single-Crystalline ZnS Nanobelts. The second example of 1D ZnS nanostructures is one of our latest works on single-crystalline ZnS nanobelts that possess sharp UV emission (≈337 nm) at RT. Single-crystalline ZnS nanobelts were synthesized by a CVD method using the same horizontal tube furnace used in the synthesis of multiangular branched ZnS nanostructures. Here, 3-nm Au layer-coated Si substrates, prepared using an electric gun deposition system (ULVAC UEP-3000-2C), were placed at the downstream position of the source material as a deposition substrate. The tube furnace was thoroughly purged with high-purity Ar in order to remove traces of oxygen from the furnace. Then, the furnace was heated to 1,100 °C in 1 h and kept at this temperature for 30 min with high-purity Ar simultaneously serving as a protecting medium and carrying gas. It was conclusively found that the right selection of source materials and controlling their evaporation and agglomeration rates are the key parameters for the achievement of single-crystalline ZnS nanobelts possessing sharp UV emission at RT.

Detailed structural characterizations of the nanobelts are shown in Figure 32. SEM and TEM observations (Figures 32a and 32b) indicate that the nanobelts grow from several separated nucleation sites. All the nanobelts seem to be connected. They have the typical widths in the range of 200 nm to 1 μm and the length can be up to a millimeter. The nanobelts cover the entire substrate and their yield varies from place to place dependent on local temperature. The highly crystalline nature of the nanobelts was further verified by an enlarged lattice-resolved HRTEM image and ED pattern, as shown in Figures 32c and 32d. The marked interplanar d-spacings of 0.63 and 0.33 nm correspond to the (0001) and (01-10) lattice planes of a wurtzite ZnS. Figure 32e illustrates a model of the nanobelts and their enclosing facets. Most of the belts take the [01-10] orientation as the growth direction and the ±(−2110) and ±(0001) planes as the top/bottom and side surfaces, respectively. The corresponding atomic model is displayed in Figure 32f. This reveals that the side surfaces are polar and are terminated either with Zn or S.
FIG. 29. (a) SEM image of a ZnS multiangular branched nanostructure with needle-shaped tips. (b) CL spectrum recorded at RT from the structure shown in (a). The inset shows the enlarged spectrum in the bandgap region. (c) and (d) CL images of the same nanostructure recorded at 334 and 404 nm, respectively. Reproduced from Fang et al. Copyright © 2008, American Chemical Society.

FIG. 30. (a) SEM image of another ZnS multiangular branched nanostructure, (b) its CL spectrum recorded at RT, (c) and (d) the corresponding CL images of the same nanostructure recorded at 333 and 400 nm, respectively. Reproduced from Fang et al. Copyright © 2008, American Chemical Society.
It is easy to note that the growth of the present ZnS nanobelts occurs with a nonpolar surface dominating the crystallization, though the polar surfaces play an important role in determining the final morphology.\(^5\)

By dispersing individual ZnS nanobelts on standard C-coated TEM copper grids, CL properties from individual ZnS nanobelts were investigated with a nanometer-scale resolution. Figures 33a and 33b display a typical SEM image and the corresponding CL image of a ZnS nanobelt. The CL spectrum shows fairly uniform luminescence that arises from the nanobelt alone. The CL spectrum acquired from an individual ZnS nanobelt (seen in the SEM image in Figure 33a) is shown in Figure 33c. This is composed of a narrow and strong UV peak centered on $\approx 337$ nm and broad low-intensity luminescence in the visible region ($\approx 550$ nm). It is noted that the present UV peak is sharper than the UV emissions reported for other 1D ZnO nanostructures. Figure 33d plots a number of CL spectra, acquired at various spots along the line shown in Figure 33a. The shapes of
CL spectra are fairly uniform. All the peaks are located at the same positions, and the intensities of the UV peaks are slightly decreased.\textsuperscript{119}

Based on the two examples above, we learned that the structure and crystallography within a given nanomaterial could vary (except the case of perfect single-crystalline nanostructures) and these can further tune the optical properties. Our experimental results demonstrate that it is possible to achieve the strong UV emission and suppression of the defect-related visible emission of 1D ZnS nanostructures at RT by elaborating the experimental processes. Note that no external sulfur source was used and control of the evaporation of source materials was the only demanding parameter.

3.2. ZnS Nanobelts as UV Light Sensors

3.2.1. Individual ZnS Nanobelt-Based UV Light Sensors

Single-crystalline ZnS nanobelts with sharp UV emission at RT have recently been assembled as UV sensors. Experimental measurements suggest that the high spectral selectivity combined with high photosensitivity and fast time response justify the effective utilization of the present ZnS nanobelts as visible-blind UV photodetectors in different areas.\textsuperscript{119}

Figure 34a shows an optical micrograph of individual ZnS nanobelt-based UV sensors. A schematic and a representative SEM image of a single-crystalline ZnS nanobelt device are displayed in Figures 34b and 34c (taken from the marked part in Figure 34a), respectively. For the fabrication of an individual nanobelt-based UV sensor, ZnS nanobelts were dispersed on a thermally oxidized Si substrate covered with a 300-nm SiO\textsubscript{2} layer. The Cr/Au (10 nm/100 nm) interdigitated electrodes were patterned on top of the nanobelts using optical lithography with the assistance of a predesigned mask and electron-beam deposition. A predesigned patterned substrate produced using the same fabrication process and the analogous electrodes were also used to fabricate a sensor made of multiple ZnS nanobelts. The gap between electrodes could be tuned while using different masks. An individual ZnS nanobelt-based sensor with Cr/Au parallel electrodes (4 μm apart) is seen in Figure 34b. The nanobelt in Figure 34c has a typical width and thickness of ~400 and ~20 nm, respectively. The uncovered part of the nanobelt is exposed to the incident light. Two typical I-V characteristics of the sensor illuminated with the light of different wavelengths of 320 and 600 nm, respectively, are shown in Figure 34d. It is easy to note that the resistance decreased by several orders of magnitude upon 320-nm light illumination compared with the sub-bandgap light with a wavelength of 600 nm. Moreover, it should be particularly highlighted that a dark current, which is
the current measured in the absence of external light, for all the
individual nanobelt-based devices was below the detection limit
(10^{-14} \text{ A}) of a current meter. The spectral response at 320 nm
is \sim 0.12 \text{ A/W} at a 5-V bias. This corresponds to an external
quantum efficiency of around 50%, if a photoconductive gain is
assumed to be 1. The present performance is comparable with
a near-UV photodetector based on the hybrid polymer/zinc ox-
ide nanorods prepared by low-temperature solution processes.
The latter device exhibited a response of 0.18 A/W at 300 nm
by applying a bias of \sim 2 \text{ V}.^{120} A spectral photoresponse of an
individual ZnS nanobelt-based UV sensor for a bias of 10 \text{ V} at
different wavelengths from 300 to 630 nm is demonstrated in
Figure 34e. The highest sensitivity was observed at the wave-
length of \sim 300 nm. A photoresponse of the sensor increased
by over 3 orders of magnitude upon illumination with a 320-nm
light compared to its response to a visible light. The high spectral
selectivity combined with the high photosensitivity implies the
bright prospects of using the present ZnS nanobelts as visible-
blind UV photodetectors in many areas. Attention should be
drawn to a particular advantage of the ZnS belt sensors: they
are stable at much higher operating temperatures compared to
standard sensors. Hence, the present detectors can be effect-
ively used for combustion monitoring of gases during which the
UV emission is a characteristic process. Figure 34f shows
a time response of the device upon 320-nm light illumination
measured for light-on and light-off conditions at a 10-V ap-
plied voltage. This shows a fast time response (<0.3 s) and very
good photocurrent reproducibility and stability. Compared with
other nanostructures-based optical sensors made of ZnO, GaN,
CdS, Ga_2O_3, TiO_2, and ZnSnO_3, the present ZnS sensors show
a faster time response both on rise and decay.^{85,93,121–128}
For example, one of the latest reports on an ultralong ZnO bridging
nanowires-based UV detector showed that the rise time (the authors
defined it as the time for the current to rise to 90% of the
peak value) was 0.7 s and the decay time (the authors defined it
as the time for the current to decay to 10% of the peak value) was
1.4 s under a typical irradiance of 10 \mu \text{ W cm}^{-2}.^{93} Some works
even found that a decay time is up to 100 s for ZnO nanowires-
based UV-light photodetectors. It is worth noting that the latter
detectors are prone to surface absorption/desorption processes.
These degrade the overall photoresponse performance.^{121}

3.2.2. Multiple ZnS Nanobelts-Based UV Light Sensors

Enhanced stability and sensitivity of the UV sensors made
of multiple ZnS nanobelt devices compared to the individual
nanobelt-based sensors was further demonstrated.\textsuperscript{119} Figure 35
illustrates a multiple ZnS nanobelts-based sensor and its perfor-
ance. The fabrication processes of the multiple ZnS nanobelts-
based sensors did not presume the predispersion on a substrate.
The process was totally different from the preparation of the in-
dividual ZnS nanobelt-based sensors. The latter nanobelts were
grown directly from the prepatterned substrate within a CVD
system (same as described above) above. Figure 35a displays
an optical image of the prepatterned substrate, which was fab-
ricated using optical lithography with the assistance of a pre-
designed mask and electron-beam deposition. (b) A high-magnification optical image of the as-grown devices
grown directly from the prepatterned substrate within a CVD
system. (c) A spectral photoresponse measured at a bias of 10 \text{ V}
in 230- to 630-nm wavelengths. (d) A time-dependent photocurrent response under 320-nm UV light illumination for
the light-on and light-off states at an applied voltage of 10 \text{ V}. Reproduced from Fang et al.\textsuperscript{119} Copyright © 2009, Wiley-VCH.
100-electrodes were repeatedly electron-beam deposited through a Au catalytic layer during the growth, the Cr/Au (10 nm/100 nm) touch both of the two neighboring electrodes forming one aligned nanostructures. The nanobelt lengths were enough to additionally grew on the top and side surfaces of the electrodes. The spaces between electrodes were densely filled with well-distributed functional electronic devices.108 Attracted considerable attention for the realization of multicomponent system functional electronic devices, including core/shell nanostructures and heterostructures, have achieved via a simple one-step thermal evaporation method or ZnS-ZnO biaxial nanobelt heterostructures and the first observation on a novel UV emission peak at ~355 nm along with normal ZnS or ZnO band-edge emissions is highlighted below.61

4. ZnS/ZnO COMPOSITE NANOSTRUCTURES

The embodiment of ZnO and ZnS nanostructures is another area of importance. The ZnS/ZnO composite nanostructures, including core/shell nanostructures and heterostructures, have attracted considerable attention for the realization of multicomponent system functional electronic devices.108,114,129–133 Recent advances in the design and control of heterostructures and superlattices in 1D nanoscale semiconductors have opened the door to new device concepts. One-dimensional heterostructures consisting of two or even more important functional materials are of prime importance for revealing unique properties. They are also essential for developing potential optoelectronic and optoelectronic devices.129 For example, Schrier et al.130 have theoretically demonstrated that the formation of ZnO/ZnS and ZnO/ZnTe nano-heterostructures can substantially reduce the optical bandgap while simultaneously maintaining the required optical absorption. They proposed that planar ZnO/ZnS and ZnO/ZnTe quantum-well heterostructures should be used for potential photovoltaic devices. The theoretical limits of ideal solar cell efficiencies for these composite nanostructures have a dramatic improvement over bulk ZnO. The authors also found dark exciton formation in the ZnO/ZnS nanowire that could improve the carrier collection in solar cells by reducing the exciton recombination rate.130 Chen et al.131 have reported that heterostructured ZnO/ZnS core-shell nanotube arrays with the diameters of 50–80 nm and lengths up to 1 µm can be synthesized by a two-step chemical reaction. PL measurement shows that the relative-intensity ratio of UV emission (I_UV) to deep-level emission (I_DLE) for ZnO/ZnS core-shell nanotubes can be enhanced by 9 times compared to original ZnO nanotubes.131 Yu et al.133 investigated two-photon-excited PL dynamics in ZnS functionalized ZnO nanotetrapods and observed that the emission peaks have a 5- to 10-nm red shift and the PL intensity and lifetime of the UV exciton radiative transition increased more than 20 times. This was suggested to be due to the passivation effect in the core/shell structure compared to the bare ZnO nanotetrapods.133 Ni et al.134 developed a hydrothermal method to achieve flower-like ZnS-ZnO heterogeneous structures. The electrochemical tests on the products showed that flower-like ZnS-ZnO heterostructures had a strong ability to promote electron transfers between H2 and the Au electrode.134 One of the latest works on the synthesis of ZnS/ZnO biaxial nanobelt heterostructures and the first observation on a novel UV emission peak centered at ~355 nm along with normal ZnS or ZnO band-edge emissions is highlighted below.61,129

A controlled synthesis of two novel semiconducting heterostructures was performed; namely, hetero-crystalline-ZnS/single-crystalline-ZnO biaxial nanobelts and side-to-side single-crystalline ZnS/ZnO biaxial nanobelts. This was achieved via a simple one-step thermal evaporation method using gold as catalyst. The typical SEM, TEM, and HRTEM images are shown in Figure 36. In the first heterostructure, a ZnS domain is composed of the heterocrystalline superlattice (3C − ZnS)N/(2H − ZnS)M[111] − [0001] (where N and M are the numbers of the atomic layers in the ZB and WZ ZnS sections) with an atomically smooth interface between wurtzite (WZ) and zinc blende (ZB) ZnS fragments. The alternating growth of WZ-ZnS/ZnO and ZB-ZnS/ZnO interfaces might reduce the stresses and system energy, leading to the formation of heterocrystalline-ZnS/single-crystalline-ZnO biaxial nanobelts. It was found that the length of 26 layers (Ls) on the WZ ZnS side is slightly larger than the distance of 19 Ls on the ZnO side, whereas the other segment 11 Ls on the ZB ZnS side is slightly smaller than the distance of 10 Ls on the ZnO side. This alternating growth makes these structures stable. For side-to-side single-crystalline ZnS/ZnO biaxial nanobelts, both parts are single crystals having a uniform interface between them.61

High-spatial-resolution CL studies on individual heterostructures reveal for the first time a new UV emission peak (~355 nm) at LT (~30 K). Such a peak cannot be observed in individual and pure ZnS or ZnO nanostructures. Figure 37 depicts typical CL spectra obtained at RT and LT from an individual heterocrystalline-ZnS/single-crystalline-ZnO biaxial nanobelt (SEM image is shown in Figure 37a). Figure 37b is an enlarged portion of the sharp UV emission bands between 310 and 430 nm. In the UV region, it is easy to see that curve 1 is composed of a very weak sharp UV emission band centered at ~345 nm, whereas a relatively strong and sharp UV emission band centered at ~385 nm is apparent for curve 2. These

observations are consistent with an expected half-ZnS/half-ZnO morphology. Figure 37c displays two representative CL spectra obtained at ~30 K from an individual heterocrystalline-ZnS/single-crystalline-ZnO biaxial nanobelt and a pure ZnS nanobelt between 310 and 430 nm. This is the first report on the new CL peak in a ZnS/ZnO composite nanostructure. It has never been observed in individual 1D ZnS and/or ZnO nanostuctures. Based on the compositional data and structural characterizations, the new peak was assigned to the presence of the special ZnS/ZnO interface. It could be a Zn-O-S ternary phase or an oxygen-doped ZnS nanostructure.61 Although the practical designs of laser and photodetector based on these hererostructures are still ongoing, they are expected to become valuable not only with respect to fundamental research but also for new broad-range UV high-performance nanoscale lasers and sensors.

5. OTHER 1D NANOSTRUCTURES

Besides ZnO and ZnS,135,136 gallium nitride (GaN, ∼3.4 eV), titanium dioxide (TiO2, ∼3.2 eV), tin dioxide (SnO2, ∼3.6 eV), indium oxide (In2O3, ∼3.6 eV), monoclinic gallium oxide (β-Ga2O3, ∼4.8 eV), aluminum nitride (AlN, ∼6.2 eV), diamond (∼5.5 eV) and their composites are other wide bandgap semiconductors that have attracted much research interest in the field of UV-light emissions, lasers, and sensors.137−144 For GaN, the stimulated emission from bulk GaN at low temperatures was reported in the 1970s,145 followed by the achievement of RT lasing in thin films in the early 1990s146 and recent production of single GaN nanowire lasers. Plenty of works have been carried out to explore GaN nanostructures for use in electrically pumped UV-blue light-emitting diodes, lasers, and photodetectors.138−140 For example, Johnson et al.138 reported the first UV-blue laser action in a single monocrystalline GaN nanowire using both near-field and far-field optical microscopy at RT radiation. The authors also claimed that the aspect ratio of these nanolasers (>250:1) was significantly larger than for ZnO nanolasers and, theoretically, lasing could be observed in smaller-diameter wires (<70 nm), although coupling of PL into lasing modes instead of radiation modes is expected to decrease with d < λ due to intrinsic diffraction effects.138 Subsequently, a simple, one-step CVD process for making quantum-wire lasers based on the Al-Ga-N system was proposed. A novel quantum-wire-in-optical-fiber (Qwof) nanostructure was obtained as a result of spontaneous Al-Ga-N phase separation at the nanometer scale and in one dimension. The simultaneous excitonic and photonic confinement within these coaxial Qwof nanostructures led to the first GaN-based quantum wire UV lasers with a relatively low threshold. These results suggest that the spontaneous phase separation in the nanowires could be driven by the intrinsic stresses. At the same time it implies that nano/heterostructures consisting of two or more important functional materials are essential for developing potential nanoelectronic and optoelectronic devices. This is governed by utilizing their capabilities of simultaneous photon, exciton, and carrier confinement.139 For GaN nanostructures-based photodetectors, Chen et al. not only achieved ultrahigh photocurrent gain in m-axial GaN nanowires147 but demonstrated a viable nanobridge device by direct integration of a GaN nanowire onto a microchip with an ultrahigh photocurrent responsivity to UV irradiation.140

Diamond is also promising for deep-UV (DUV) photoelectronics applications due to its large bandgap, large exciton energy (80 meV) and radiation robustness. However, its development is far behind SiC- and GaN-based semiconductors due to the difficulty in making large-area diamond single crystals with controlled doping level. In 2001, the first p-n junction DUV LEDs was demonstrated by Koizumi et al. on a (111)-oriented single crystal diamond epilayer.148 Due to the deep nature of the donor phosphorus and the deep defects in the epitaxial layers, both the emission efficiency and the diode spectrum needed improvement. Lately, diamond detectors have evidenced significant progress due to the development of microwave
plasma CVD technology and are now commercially available. Three-dimensional nanostructured diamond offers the advantage of large-area production. However, its utilization in photoelectronics suffers from both fundamental and technical problems such as electrical conductivity control, impurities, and grain boundaries; these factors negatively affect the performance. The works on self-assembled 1D single-crystal diamond nanostructures are still limited and are rather challenging. To achieve photoelectronics applications of 1D diamond nanostructures, novel concepts both in synthesis and device physics are required.

6. CONCLUSIONS AND OUTLOOK

Recent developments in our understanding of UV-light emissions, lasers, and sensors based on ZnO and ZnS nanostructures have particularly been highlighted in this review. We focused on 1D ZnO and ZnS nanostructures. Needless to say, due to space limitations, this article is unable to list all the exciting works reported in this field. Although our present investigations are only a part of main studies on ZnO and ZnS nanostructures for applications, the above discussions show that ZnO and ZnS nanostructures have become one of the most popular research pursuits in the field of materials science due to their intriguing properties and wide range of possible applications. The fascinating achievements in new device concepts should inspire more research efforts to meet the demands of novel nanoscale photodectors, lasers, and other devices based on ZnO and ZnS nanomaterials.

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