

# A Critique on Synthesis of 1-D Nanostructure of ZnS and its Potential Applications

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**Abstract**—Zinc sulphide is an important II-IV semiconductor material with a wide band gap. It exhibits better chemical stability compared to other chalcogenides material due to which it has numerous applications such as LEDs, FETs, Solar cells etc. ZnS can have two different crystal structures (Zinc Blende and Wurtzite), both being direct band structures. In recent years, nano-crystalline ZnS has attracted much attention because properties in nano-regime differ considerably from those of their bulk counterparts.

Therefore, much effort has been made to control the size, morphology and crystallinity of the ZnS nanostructure with a view of tuning their physical, electrical and chemical properties. Recent trends in nanomaterials research mainly focus on One-dimensional inorganic nanostructures due to their potential for understanding fundamental physical concepts and constructing nanoscale electronic and optoelectronic devices. This critical review mainly focuses on our recent research progresses in 1D ZnS nanostructures, including their different synthesis process and potential applications, with an emphasis on solar cell applications. Finally, this review is concluded with some perspectives and future research scope in these fields.

## 1. INTRODUCTION

One-dimensional (1D) nanostructures possess fascinating physical properties determined by their special shapes and structures and have wide applications in solar energy conversion, thermoelectric devices, energy storage technology, and so forth[1].

ZnS is a commercially important II–VI semiconductor. It has a wide optical direct band gap, which makes it a very attractive material for optical applications, especially in nano crystalline form. It is very less toxic, highly transparent and cost effective[2]. After the discovery of pure carbon nanotubes, intensive research moulded more towards one dimensional nanometre scale materials to be aware of its the novel physical properties [1].

To deal with the rising energy and environmental problems, considerable research has been stimulated on preparation technologies of novel 1D nanostructures and exploring their energy applications[3].

Moreover, one-dimensional nanostructures were reported to exhibit better charge transport and lower recombination than the nanoparticles in liquid dye-sensitized solar cells (DSC)[4].

Low-dimensional nanostructured materials have drawn much attention because of their basic roles in order to understand the quantum size effect and vast applications in light-emitting diodes, gas sensors, nano thermometers, solar cells, fuel cells, piezoelectric nanogenerators and lithium-ion batteries. ZnS can also serve as an important semiconductor photocatalyst to remove toxic or organic water pollutants owing to the highly negative reduction potentials of excited electrons and the rapid generation of electron–hole pairs[5].

One dimensional nanostructure are one of important morphology in the field of nanotechnology as it can present direct electrical pathways for photogenerated electrons to increase the electron transport rate so that it is very potential candidate for the use in solar cells for better efficiency. The efficient electron transport is ascribed to considerably decreased intercrystalline contact points and specified directionality[6].

Because of the above mentioned significance and various applications of 1-D nanostructures. There is an extreme need to grow 1-D nanostructure in plenty to utilise its importance. In principle; it is feasible to make any solid material into 1D nanostructures by controlling precisely the synthesis conditions[7]. In this review article different synthesis methods i.e by evaporation of ZnS nanoparticles[1], Solvothermal synthesis[8], Hydrothermal method followed by mild thermolysis of covalent organic-inorganic network[9], plasma assisted chemical vapour deposition[10], field emission from ZnS nanorods by Radio frequency magnetron sputtering technique on glass and Si substrates[11], Thermal evaporation[12], Microwave irradiation, by sulfidation of aligned ZnO nanorod arrays[13], precipitation method using PEG[14] and their potential applications

## 2. SYNTHESIS METHODS

### Evaoparation of ZnS nanopowders

Xiao-Sheng Fang et al reported the temperature controlled catalytic growth of 1-d nanostructure by the evaporation of ZnS nanopowders; the synthesis was conducted in tube furnace with 20mm inner-diameter alumina tube mounted inside. Homemade ZnS powders were placed in alumina boat and then put into the center of alumina boat. During the heating process there was a flow of Ar gas kept at 80 sccm.[1].

### Solvothermal approach

Subhajit Biswas et al reported solvothermal approach for the synthesis of ZnS Nanocrystals, In the solvothermal process, the decomposition of the precursors in a particular solvent depends on the temperature and pressure within the reaction vessel and the pressure was related to the filling fraction of the solvent. It is a single and simple synthesis approach in which a Teflon-lined stainless steel cylindrical closed chamber with 100 ml capacity was used. In the solvothermal process the solvent plays the most crucial role in determining the size, shape and crystal structure of the final products[15].

### Mild thermolysis of covalent-organic inorganic network

Xijian jhen et al reported the synthesis using Mild thermolysis of covalent-organic inorganic network, in this method neither any liquid crystal templates nor hard porous templates, but based on the thermolysis of a novel lamellar covalent organic-inorganic hybrid chalcogenide in which solution of precursors were put into a Teflon cup and magnetically stirred. The Teflon-lined autoclave was sealed tightly and maintained at a certain temperature for hours, and then cooled to ambient temperature naturally. A product was obtained through filtering, and then washed by alcohol and distilled water, respectively, to remove impurities and then the thermolysis of ZnS 0.5en in aqueous solution was performed in a closed autoclave[9].

### Plasma-assisted metal organic chemical vapor deposition

Q.J. Feng et al reported Plasma-assisted metal organic chemical vapour for the synthesis of 1D growth of ZnS nanoparticles ZnS nanorods were grown on c-plane Al<sub>2</sub>O<sub>3</sub> substrates by a self-assemble P-MOCVD system at substrate temperature of 650°C without employing any metal catalyst. The plasma of our MOCVD equipment was produced by high frequency inductive loop, which enlaced outside quartz growth chamber. This high-frequency loop could heat up substrates. And plasma generation depended strongly on both growth temperature and reactor pressure. It is a catalyst-free method. It was found that the plasma plays an important role in the growth process and results in change of morphology of ZnS.[10].

### Radio frequency magnetron sputtering technique

P.K. Ghosh et al used radio frequency magnetron sputtering technique for the 1-D nanostructure of ZnS nanoparticles Zinc sulfide (ZnS) target was fabricated by taking a suitable aluminium holder (2 in. diameter), The fabricated ZnS target was placed in the radio frequency magnetron sputtering (13.56 MHz) chamber for the deposition of nanocrystalline thin films on various substrates such as glass and Si[11].

### Annealing precursor ZnS nanoparticles in NaCl flux

Chun Lan et al used Annealing precursor ZnS nanoparticles in NaCl flux, This method requires neither complex apparatus and sophisticated techniques nor metal catalysts and/or templates as usually needed in other methods. Adding NaCl can provide a favorable environment for the growth of nanorod. It is novel and simple synthetic route in which ZnS nanorods were synthesized by annealing precursor ZnS nanoparticles, which were prepared by one-step, solid-state reaction of ZnCl<sub>2</sub> and Na<sub>2</sub>S through grinding by hand at ambient temperature, in NaCl flux[16].

### Thermal Evaporation

Changhao Liang et al utilised Au-Mediated Growth of Wurtzite ZnS Nanorods via Thermal Evaporation, simple thermal evaporation of ZnS powder at a relatively lower temperature of 970 °C in the presence of Au catalysts was done A high-temperature horizontal tube furnace (SiC heater) was used to synthesize the ZnS nanostructures. Zinc Sulfide powder (99.99% pure) was loaded into a ceramic boat that was positioned inside the ceramic tube and placed in the center of the furnace[12].

### Microwave Irradiation

Mukta V Limaye et al reported Template-free ZnS nanorod synthesis by microwave irradiation where a simple, multimode microwave reactor was used. Various interesting characteristics of microwaves make them a suitable agent for promoting chemical reactions. The well-defined frequency of microwave radiation allows it to be active for selected bonds, providing selective (and tunable) heating. Rapid heating rates and simultaneous heating result in reduced reaction times, higher yields and better homogeneity of the products.[13].

### Sulfidation of Aligned ZnO Nanorod Arrays

Subhendu K. Panda et al reported Fabrication of ZnS Nanorod Arrays by Sulfidation of Aligned ZnO Nanorod Arrays The complete conversion of ZnO nanorods to ZnS nanorods was carried out at 600 °C in an atmosphere of an H<sub>2</sub>S and argon mixture of 1:20 at atmospheric pressure. Typically, after 2 h of exposure to H<sub>2</sub>S, fully converted ZnS nanorods were obtained without breaking the alignment the ability to choose the crystallographic growth direction of a nanorod array aids in tuning the physical properties of the material, including spontaneous piezoelectric polarization, thermal and electrical

conductivity, dielectric constant, lattice strain, and so forth[17].

### Aqua-solution hydrothermal process upon pulse-plating Zn nanocrystallines

Wen Yu et al reported ZnS nanorod arrays synthesized by an aqua-solution hydrothermal process upon pulse-plating Zn nanocrystallines. Typically, Zn nanocrystallines were pulse-plated on a pure copper substrate. The aqua-solution pH value was adjusted to 10 by adding 3 M sodium hydroxide (NaOH) solution. This method involves neither template nor surfactant.[18].

### Nanorods using a single-source molecular precursor

Yong Cai Zhang et al Adopting Zn-(DDTC)<sub>2</sub> as the single-source molecular precursor, Hydrazine hydrate used as the solvent. The single-source molecular precursor (an individual molecule containing all the elements required in the final product) route has several appealing features. First of all, it offers the potential advantages of mildness, safety and simplified fabrication procedure and equipment, when compared with the use of multiple sources requiring exact control over stoichiometry [8].

### From a single block copolymer

Zhigang Zhao et al reported the synthesis of ZnS nanostructures with morphology of nanorods from a single block copolymer. Aqueous reaction system under mild conditions was done by simply changing the synthesis routes. This simple synthesis strategy may be comprehensive to the shape-controlled production of nanostructures of other inorganic materials. It is an effective shape control of ZnS from a single reaction system.[19]

### Precipitation method

Dan-Jie Zhou et al reported facile synthesis of ZnS nanorods in PEG (Poly ethylene glycol), as a structure-directing agent was used. It is a simple, cost-effective method, lesser time taking and facile technique [14].

## 3. APPLICATIONS

In the nanoscale region, the phase, morphology and size of ZnS strongly influence its physical and chemical properties. For practical applications in the future optoelectronic nanodevices, the preparation of one-dimensional (1D)[7], W-ZnS nanostructures such as nanorods, nanowires, nanotubes, etc., are generally desirable on one hand, W-ZnS, the high temperature stable form of ZnS crystal, can easily meet the basic requirement of thermal stability for reliable optoelectronic device operation; on the other hand, 1D nanostructures may exhibit a variety of shape- and size-dependent electric and optical properties and serve as good building blocks in constructing many novel functional materials via the so-called “bottom-up” approach[8]. Well

aligned one-dimensional nanostructures on substrates are highly attractive for device applications in particular. Such 1D devices are of immense research interest due to their special properties arising out of quantum confinement effects in the radial direction, in spite of their macroscopic lengths. Technologically, these materials are potential candidates for applications such as connectors/conductors in nanodevice chips and field emitters.

ZnS nanostructures are used as buffer layers in thin film solar cells. They are highly used in electroluminescent devices, light emitting diodes, antireflection coatings, lasers, low voltage cathodoluminescent display devices, bio sensors, DNA markers, multilayer dielectric filters, and also it is an efficient phosphor in flat panel displays. ZnS has also been used as a passivation layer in the preparation of quantum dots and can be used in diodes, field effect transistors, electro-optic modulators etc[15].

**Table 1: Precursors used in methods**

S.No.	Methods	Precursors used:
1.	Evaoparation of ZnS nanopowders	ZnS naopowder
2.	Solvothermal approach	zinc nitrate (Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O) or zinc acetate ((CH <sub>3</sub> COO) <sub>2</sub> Zn)and thiourea (tu, NH <sub>2</sub> CSNH <sub>2</sub> ), Ethylenediamine (EN), ethylenediamine–water (EN–W) mixed in different volumetric ratios, water (W), ethylene glycol (EG), ethanol (E) and benzene (B)
3.	Mild thermolysis of covalent-organic inorganic network	zinc acetate [Zn(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O] and thiourea [SC(NH <sub>2</sub> ) <sub>2</sub> ], water, ethylenediamine(en)
4.	Plasma-assisted metalorganic chemical vapor deposition	Dimethylzinc (DMZn) and H <sub>2</sub> S
5.	Radio frequency magnetron sputtering technique	aluminium holder (2 in. diameter) and ZnS polycrystalline powder (99.99%, Aldrich)
6.	Annealing precursor ZnS nanoparticles in NaCl flux	ZnCl <sub>2</sub> , Na <sub>2</sub> S·9H <sub>2</sub> O and C <sub>18</sub> H <sub>37</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>10</sub> H (C <sub>18</sub> EO <sub>10</sub> )
7.	Thermal Evaporation	Zinc sulfide powder (99.99% pure), A piece of sapphire (0001) substrate coated with Au film
8.	Microwave irradiation	Zinc chloride and thiourea, ethylenediamine
9.	Sulfidation of Aligned ZnO Nanorod Arrays	ZnO nanorods, H <sub>2</sub> S and argon mixture of 1:20 at atmospheric pressure
10.	Aqua-solution hydrothermal process upon pulse-plating Zn nanocrystallines	zinc acetate [Zn(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O], Thiourea [CS(NH <sub>2</sub> ) <sub>2</sub> ] and Cu substrate, (NaOH)

11.	Nanorods using a single-source molecular precursor	Zn-(DDTC)2
12.	From a single block copolymer	amphiphilic block copolymer surfactant, poly(ethylene oxide)-poly(propylene oxide)-poly(ethyleneoxide) (EO20PO70EO20, Pluronic P123)
13.	Precipitation method	zinc nitrate hexahydrate [Zn(NO3)2·6H2O], polyethylene glycol (PEG) 400 and anhydrous ethanol (AR)

#### 4. CONCLUSIONS

In this review article, the recent research progress in the various methods for the synthesis of 1D ZnS nanostructures have been described and its potential applications. Table-1 summarises the precursors used in different methods for the synthesis of 1-D ZnS nanostructure.

#### 5. FUTURE RESEARCH SCOPES AND PERSPECTIVES

To develop a simple, efficient and cheap technology to synthesize 1D ZnS nanostructures with high quality and large quantity, significant challenges still exist. The investigation for the growth of 1D ZnS nanostructure will be constantly stimulating and greatly rewarding. More defined control on morphology, orientation, composition, doping, crystallization and hierarchical assembly is required.

1-D nanostructures and their applications are still in the beginning stage of technical development. Undoubtedly there will be many innovations and solutions on the route towards their practical integration into nanotechnology. However, many issues need to be solved before that.

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