

Wet-Chemical Synthesis and Optical Property of ZnSe Nanowires by Ag₂Se-Catalyzed Growth Mechanism

Junli Wang^{1,2*}, Hui Feng¹, Weiling Fan¹, Kangmin Chen³, Qing Yang²

¹Scientific Research Academy and School of Chemistry & Chemical Engineering, Jiangsu University, Zhenjiang, China

²Hefei National Laboratory of Physical Sciences at the Microscale & Department of Chemistry, University of Science and Technology of China (USTC), Hefei, China

³School of Materials Science & Engineering, Jiangsu University, Zhenjiang, China
Email: *wangjl@mail.ujs.edu.cn

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ABSTRACT

High-quality II-VI semiconductor ZnSe nanowires were facilely prepared in the oleic acid and oleylamine mixed solution at low temperatures of 130°C - 200°C through an Ag₂Se-catalyzed growth mechanism. Oleylamine served as an effective reducing agent and a surfactant in the synthesis. Many of the resultant nanowires were terminated by an Ag₂Se catalyst particle at one of their ends, confirming that the nanowire growth followed a catalytic mechanism. The crystal structure of Ag₂Se catalyst was examined, which exhibited a metastable tetragonal phase, not the common orthorhombic phase. Meanwhile, the optical properties of as-synthesized ZnSe nanowire solid powder were evaluated by the UV-Visible diffuse reflectance and photoluminescence spectroscopy and a significant blue shift was observed compared to the bulk ZnSe with a band gap of 2.7 eV. This work would provide an alternative and effective catalytic route for the preparation of one-dimensional (1D) nanostructures of ZnSe and other metal selenides.

Keywords: ZnSe; Nanowires; Catalytic Growth; Ag₂Se Catalyst; Oleylamine

1. Introduction

One-dimensional (1D) semiconductor nanomaterials have drawn significant research attention due to their fundamental property versatility and broad applications in electronic and optoelectronic devices [1-3]. As an important II-VI group semiconductor with band gap of 2.70 eV, ZnSe 1D nanostructures, such as nanowires, nanorods and nanobelts, are actively studied in view of their controlled preparation, property engineering and nanodevice fabrication [3-5]. In particular, many efforts are devoted to exploring the controllable synthesis and growth mechanisms of these 1D ZnSe nanostructures with well-defined size, composition and morphology, which is still a challenge of much interest.

In the past decade, many wet-chemical methods have been developed to synthesize 1D ZnSe nanostructures, including solvothermal reaction, colloidal chemistry synthesis and solution-based catalytic route. These wet-chemical synthetic methods can be rationally designed in terms of several typical growth mechanisms. For instance, a variety of 1D nanostructures of ZnSe have been effec-

tively prepared through the template mechanism derived from coordination effect in the solvothermal synthesis, where many N-chelating compounds, including hydrazine (N₂H₄) [6] and organic small molecular amines such as n-butylamine [7], ethylenediamine (en) [8,9], and tetraethylenepentamine (TEPA) [10], are employed as coordination and directing agents. It is even found that some inorganic-organic coordination complexes formed between ZnSe and these N-ligands, such as ZnSe(N₂H₄)_x [6], ZnSe(en)_{0.5} or ZnSe(en)₃ [8,9], and ZnSe(TEPA)_{0.5} [10], act as metastable 1D soft-templates to produce ZnSe nanorods, nanobelts, nanowires or nanowire-bundles. Meanwhile, the colloidal chemistry synthesis based on surfactants or mixed surfactants, including phosphonic acids (Tri-n-octylphosphine (TOP), tri-n-butylphosphine (TBP)), long carbon-chain amines (n-octadecylamine, oleylamine) and carboxylic acids (oleic acid) [4,11-13], which can lead to the anisotropic growth of ZnSe nanocrystals by modifying the activity of different crystal facets, is effective to grow ZnSe nanorods and nanowires with small size and high uniformity. Another mechanism for the growth of 1D nanostructures is the solution-phase catalytic approaches. One well-known

*Corresponding author.

example is the Bi-catalyzed solution-liquid-solid (SLS) regime proposed by Buhro *et al.*, through which ZnSe nanowires of high length and quality are prepared [14-16]. Recently, a new catalytic mechanism, that is, Ag₂Se-catalytic growth route, has been explored for preparing ZnSe nanowires [17-19]. This route was successfully performed by our group in the mixed solution of ethanol-oleic acid or DMF-oleic acid in the presence of surfactants such as polyvinyl pyrrolidone (PVP) and oleylamine [18,19].

In this report, we develop the Ag₂Se-catalyzed synthesis of ZnSe nanowires in the mixture solution of oleic acid and oleylamine, which aims to show the good extendibility and generality of Ag₂Se-catalyzed mechanism in various reaction media (e.g., solvents, surfactants and reductants). This method is simple, inexpensive, and easy to operate and will be a good complement to the well-known solution-phase SLS [14-16] and vapor-phase VLS (vapor-liquid-solid) [20,21] catalytic mechanisms for the preparation of ZnSe nanowires.

2. Experimental Section

2.1. Nanowire Synthesis

In a typical synthetic procedure, ZnCl₂ (0.2 mmol) and SeO₂ (0.2 mmol) were added into the mixed solution of oleic acid (5 mL) and oleylamine (1 mL) in a Teflon-lined autoclave of 12 mL capacity. After stirring for several minutes, 0.5 mL of AgNO₃ EtOH solution (0.02 mmol/mL) was dropped into the above solution, which is used to produce Ag₂Se catalytic seeds by reacting with SeO₂. The autoclave containing reaction solution was sealed and kept at 130 - 200°C for 1 - 3 h. As cooled to room temperature naturally, the dark yellow products were collected by centrifugation, washed three times with ethanol, and then dried in vacuum at 50°C. ZnSe nanowires could be synthesized at various Ag/Zn molar ratios (calculated by the initially added amounts of AgNO₃ and ZnCl₂). In this study, the Ag/Zn molar ratio is typically fixed at 5% for the nanowire synthesis.

2.2. Characterization

Room temperature X-ray powder diffraction (XRD) was performed on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.54184$ Å) at a voltage/current of 40 kV/200mA and a step size of 0.02°. The XRD pattern was analyzed with a MDI Jade 6.0. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were performed on a JEOL JEM 2010 TEM at an acceleration voltage of 200 kV, which is equipped with an X-ray energy dispersive spectrometer (EDS, Oxford Inca) for the EDS analysis. UV-Visible diffuse reflectance spectrum was recorded on a Cary 50 UV-Vis spectrophotometer scanning from 200 to 800 nm.

The photoluminescence (PL) spectrum was measured using a He-Cd laser with a 325 nm as an exciting source. Both the PL and UV-Vis diffuse reflectance spectra were measured on the as-prepared ZnSe nanowire solid powder at room temperature.

3. Results and Discussion

Transmission electron microscopy (TEM) was used to examine the morphology of the product obtained from the typical synthetic procedure (see Experimental Section). As shown in **Figure 1**, the product consists of ZnSe nanowires with diameters in the range of 4 - 90 nm and length of from several hundred nanometers to several microns. Interestingly, many of the as-obtained nanowires having a darker particle loaded at their one end are observed, which shows the characteristic feature of nanowire growth in a catalytic mechanism. Our studies (described below) confirm that the darker particle is Ag₂Se and the wire is ZnSe. It is also observed that the diameters of nanowires are dependent on the size of the catalytic particles on their tips. Meanwhile, the Ag₂Se catalytic particles have a size slightly larger (5 - 13 nm) than the corresponding ZnSe nanowires in the diameter. These growth characteristics of ZnSe nanowires are well consistent with those observed in the SLS or VLS mechanism [14-16,20,21], similar to what we have found for the ZnSe nanowires obtained in the ethanol-oleic acid or DMF-oleic acid mixed reaction system [18,19], except that a broad nanowire diameter distribution is produced in this oleic acid-oleylamine system.

Figure 2(a) shows the room-temperature X-ray diffraction (XRD) pattern of the as-prepared ZnSe nanowires. The XRD pattern can be indexed to the mixed crystalline phases of ZnSe and Ag₂Se. In detail, the three strongest diffraction peaks are from cubic zinc blende ZnSe (ZB, JCPDS# 88-2345), matching well with the crystal planes of (111), (220), and (311). The relatively weak peaks marked with asterisk (*) are assigned to hexagonal wurtzite ZnSe (W, JCPDS# 89-2940). Obviously, The ZB ZnSe is dominant in the products, accompanied by a small amount of W polymorph. The XRD peaks present within the blue rectangle are assigned to crystalline Ag₂Se, which match well with tetragonal structure of lattice parameters $a = b = 7.06$ Å and $c = 4.98$ or 4.76 Å [19,22-24]. The tetragonal phase can be seen as another polymorph of Ag₂Se, besides cubic and orthorhombic crystal structures [22-24], and has a simple, direct structural transformation relation with the cubic phase (**Figure 2(c)**) [24]. If the reaction time was shortened from 3 h to 1 h, elemental selenium (Se) appears in the products while the diffractions of ZnSe and Ag₂Se are kept unchanged (**Figure S1**, see Supplement). The yield of Se can be attributed to the reduction of SeO₂ by oleylamine.

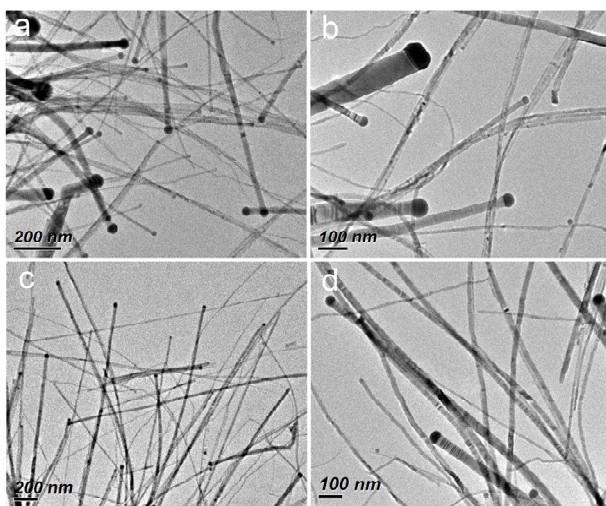


Figure 1. TEM images at different magnifications of ZnSe nanowires prepared from the typical synthetic procedure.

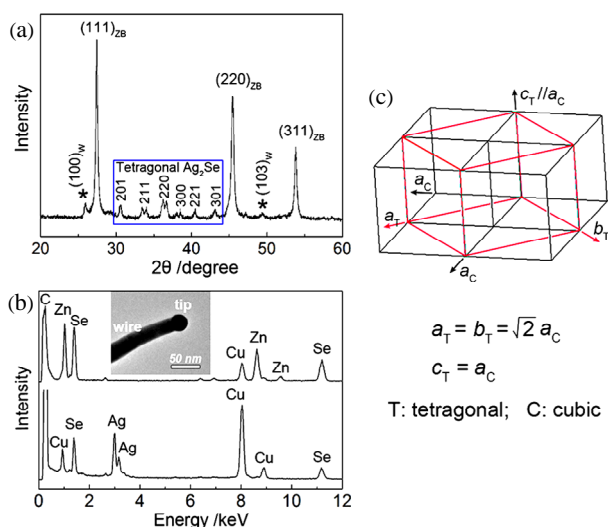


Figure 2. (a) XRD pattern of the as-prepared ZnSe nanowires. (b) EDS spectra recorded on the ZnSe wire and the Ag_2Se catalytic tip (the insets). (c) Schematic of the structural relation between cubic and tetragonal Ag_2Se .

X-ray energy dispersive spectrum (EDS) was performed to characterize the chemical compositions of the catalytic particle and the wire from a typical Ag_2Se -catalyzed ZnSe nanowire (the inset of **Figure 2(b)**). The results reveal that the dark catalytic particle is composed of Ag and Se with a measured molar ratio of 1.93:1 whereas the wire is of only Zn and Se with a molar ratio of 1.02:1 (**Figure 2(b)**). Zn signal is not detected in the tip and Ag signal not detected in the wire by EDS analysis within its detection limit. The EDS elemental analyses coupled with the XRD result confirm that the darker catalytic particle is Ag_2Se and the lighter wire is ZnSe.

The structural information of Ag_2Se catalytic particle

and ZnSe nanowire was demonstrated by using high-resolution TEM (HRTEM). As shown in the HRTEM image (**Figure 3(a)**), the well-defined lattice fringes suggest the high crystallinity of both the tip and wire parts. The crystallographic planes corresponding to the lattice fringes for the catalytic tip and the wire can be determined from their interplanar distances and fast Fourier transfer (FFT) patterns. For the wire, the measured distance between two adjacent fringes is 3.29 Å, matching well with the interplanar spacing of the cubic ZB ZnSe (1-11) planes, and the corresponding FFT pattern can be indexed to the $[-112]$ zone axis diffraction pattern, containing another spot of the (220) plane with $d = 2.00$ Å (**Figure 3(b)**). These results show that ZnSe nanowires grow along the ZB structure $[1-11]$ direction. As shown in **Figure 3(c)**, the FFT pattern of the catalytic tip can be readily assigned to tetragonal Ag_2Se with the incident electron beam parallel to the $[010]$ zone axis, in which the diffraction spots of the (002) and (200) planes are detected with interplanar spacings of 2.48 and 3.54 Å, respectively.

Recently, Connor *et al.* used Cu_2S nanocrystals as seeds to prepare CuInS_2 nanorods in solution and they suggested that at the reaction temperature of 250°C Cu_2S nanocrystals are in the superionic conducting state, which promotes the growth of CuInS_2 nanorods [25]. As reported in literature, Ag_2Se has a first-order solid-solid phase transition at 133 - 135°C from low-temperature orthorhombic semiconductor phase to high-temperature cubic superionic conductor phase [22-24,26]. In our latest report [19], we confirmed that it is the cubic superionic-phase Ag_2Se that catalyzes the growth of ZnSe nanowires in the mixed solution of DMF-oleic acid. In the current work, the used synthetic temperature is 180 - 200°C and is much higher than the temperature (133 - 135°C) of phase transition of Ag_2Se to superionic cubic phase. So, it is believed that the growth of ZnSe nanowires, performed in the oleic acid and oleylamine mixture solution, is also catalyzed by cubic superionic-phase

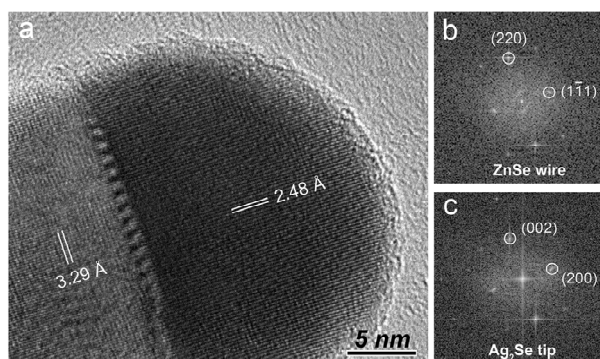


Figure 3. (a) HRTEM image of ZnSe nanowires terminated by an Ag_2Se particle and the corresponding FFT patterns for (b) ZnSe wire and (c) Ag_2Se catalytic tip.

Ag₂Se nanoparticles, like the growth of CuInS₂ nanorods catalyzed by Cu₂S [25]. Interestingly, as determined by XRD and HRTEM analyses (**Figures 2(a)** and **3**), when the reaction temperature is cooled to room temperature the high-temperature cubic phase of Ag₂Se catalytic particles is directly converted to the low-temperature tetragonal phase (**Figure 2(c)**), not the common low-temperature orthorhombic phase [26]. The formation of tetragonal phase Ag₂Se is probably due to the small grain size of Ag₂Se catalytic particles [22] and the coexisting of ZnSe [27].

The above investigations show that the Ag₂Se-catalytic route is an effective method for the synthesis of ZnSe nanowires, where Ag₂Se plays the role as Bi in the SLS mechanism [14-16] and Au in the VLS mechanism [20,21]. In the reaction solution of oleic acid and oleylamine, Ag₂Se will be precipitated out before ZnSe due to the difference in the K_{sp} values ($Ag_2Se \ll ZnSe$), which provides the preexisting catalytic particles for the growth of ZnSe nanowires. Oleylamine is used as a reducing agent in the synthesis and it can easily reduce SeO₂ to Se and AgNO₃ to Ag [28], which is confirmed our control experiments (**Figures S1** and **S2**). It is considered that Ag₂Se is produced from two reaction pathways, the reaction of Se with Ag⁺ ions and the reaction of Se with Ag, leading to a broad size distribution of Ag₂Se catalytic seeds and thus ZnSe nanowires with a large range in the diameters (**Figure 1**). The control over the uniformity of nanowires is worthy of further study.

Shown in **Figure 4** are the UV-Vis diffuse reflectance and photoluminescence (PL) spectra of the as-obtained ZnSe nanowire solid powder. An obvious absorption in the region below 450 nm is detected and the absorption edge (reflectance threshold) is measured at 442 nm, corresponding to a band gap of 2.81 eV. This value is blue shifted by 0.11 eV from that of bulk ZnSe (2.7 eV, 460 nm) [3]. The PL spectrum of ZnSe nanowires shows a

strong, sharp emission peak centered at 414 nm (2.99 eV). To our knowledge, such a significantly blue-shifted PL peak has not reported previously, although this emission is usually related to the near-band-edge (NBE) emission of ZnSe [10,17,29,30]. The reasons for the remarkable blue shift in the UV-Vis absorption and PL emission are not deeply studied and may be the excitation and recombination of excitons trapped by the charged centers at the nanowire surfaces and/or the quantum confinement effect derived from the thin ZnSe nanowires with diameters below Bohr diameter of ~9.0 nm [13]. Meanwhile, a weak broad emission between 500 - 600 nm is also observed, probably due to the Ag-related donor-acceptor pair (DAP) [29,30] luminescence arising from the Ag doping in ZnSe caused by the diffusion of Ag⁺ ions.

4. Conclusion

In summary, we have extended the wet-chemical catalytic synthesis of ZnSe nanowires in the mixed solution of oleic acid and oleylamine via a catalytic growth mechanism. Ag₂Se seeds exhibit excellent catalytic ability for the growth of ZnSe nanowires like Au catalyst in the VLS mechanism and Bi catalyst in the SLS mechanism. The obtained nanowires have been carefully characterized and their UV-Vis diffuse reflectance and PL emission properties are studied. This work provides an alternative catalytic route for synthesizing ZnSe nanowires and would be helpful to the preparation of 1D nanostructures of other metal selenides, which may find their potential use in electronic and/or optoelectronic devices.

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REFERENCES

- [1] R. Yan, D. Gargas and P. Yang, "Nanowire Photonics," *Nature Photonics*, Vol. 3, No. 10, 2009, pp. 569-576. <http://dx.doi.org/10.1038/nphoton.2009.184>
- [2] T. Cohen-Karni and C. M. Lieber, "Nanowire Nanoelectronics: Building Interfaces with Tissue and Cells at the Natural Scale of Biology," *Pure and Applied Chemistry*, Vol. 85, No. 5, 2013, pp. 883-901. <http://dx.doi.org/10.1351/PAC-CON-12-10-19>
- [3] T. Zhai, L. Li, X. Wang, X. Fang, Y. Bando and D. Golberg, "Recent Developments in One-Dimensional Inorganic Nanostructures for Photodetectors," *Advanced Functional Materials*, Vol. 20, No. 24, 2010, pp. 4233-4248. <http://dx.doi.org/10.1002/adfm.201001259>
- [4] S. Acharya, S. Sarkar and N. Pradhan, "Material Diffusion and Doping of Mn in Wurtzite ZnSe Nanorods," *The*

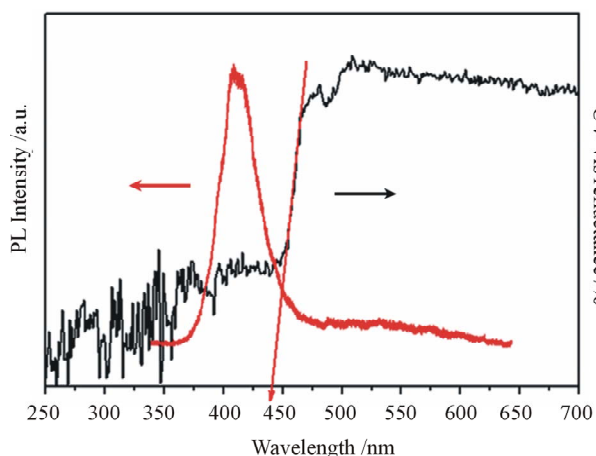


Figure 4. Room temperature UV-vis diffuse reflectance and PL spectra of ZnSe nanowires.

- Journal of Physical Chemistry C*, Vol. 117, No. 11, 2013, pp. 6006-6012. <http://dx.doi.org/10.1021/jp400456t>
- [5] L. Wang, M. Lu, X. Wang, Y. Yu, X. Zhao, P. Lv, H. Song, X. Zhang, L. Luo, C. Wu, Y. Zhang and J. Jie, "Tuning the p-Type Conductivity of ZnSe Nanowires via Silver Doping for Rectifying and Photovoltaic Device Applications," *Journal of Materials Chemistry A*, Vol. 1, No. 4, 2013, pp. 1148-1154. <http://dx.doi.org/10.1039/c2ta00471b>
 - [6] Y. Dong, Q. Peng and Y. Li, "Semiconductor Zinc Chalcogenides Nanofibers from 1-D Molecular Precursors," *Inorganic Chemistry Communications*, Vol. 7, No. 3, 2004, pp. 370-373. <http://dx.doi.org/10.1016/j.inoche.2003.12.017>
 - [7] J. Yang, C. Xue, S. H. Yu, J. H. Zeng and Y. T. Qian, "General Synthesis of Semiconductor Chalcogenide Nanorods by Using the Monodentate Ligand n-Butylamine as a Shape Controller," *Angewandte Chemie International Edition*, Vol. 41, No. 24, 2002, pp. 4697-4700. <http://dx.doi.org/10.1002/anie.200290020>
 - [8] Z. Deng, C. Wang, X. Sun and Y. Li, "Structure-Directing Coordination Template Effect of Ethylenediamine in Formations of ZnS and ZnSe Nanocrystallites via Solvothermal Route," *Inorganic Chemistry*, Vol. 41, No. 4, 2002, pp. 869-873. <http://dx.doi.org/10.1021/ic0103502>
 - [9] S. L. Xiong, J. M. Shen, Q. Xie, Y. Q. Gao, Q. Tang and Y. T. Qian, "A Precursor-Based Route to ZnSe Nanowire Bundles," *Advanced Functional Materials*, Vol. 15, No. 11, 2005, pp. 1787-1792. <http://dx.doi.org/10.1002/adfm.200500069>
 - [10] B. Xi, S. L. Xiong, D. Xu, J. Li, H. Zhou, J. Pan, J. Li and Y. T. Qian, "Tetraethylenepentamine-Directed Controllable Synthesis of Wurtzite ZnSe Nanostructures with Tunable Morphology," *Chemistry-A European Journal*, Vol. 14, No. 31, 2008, pp. 9786-9791. <http://dx.doi.org/10.1002/chem.200801041>
 - [11] L. S. Li, N. Pradhan, Y. Wang and X. Peng, "High Quality ZnSe and ZnS Nanocrystals Formed by Activating Zinc Carboxylate Precursors," *Nano Letters*, Vol. 4, No. 11, 2004, pp. 2261-2264. <http://dx.doi.org/10.1021/nl048650e>
 - [12] A. B. Panda, S. Acharya and S. Efrima, "Ultrathin ZnSe Nanorods and Nanowires: Structure, Spectroscopy, and One-Dimensional Properties," *Advanced Materials*, Vol. 17, No. 20, 2005, pp. 2471-2474. <http://dx.doi.org/10.1002/adma.200500551>
 - [13] T. Yao, Q. Zhao, Z. Qiao, F. Peng, H. Wang, H. Yu, C. Chi and J. Yang, "Chemical Synthesis, Structural Characterization, Optical Properties, and Photocatalytic Activity of Ultrathin ZnSe Nanorods," *Chemistry-A European Journal*, Vol. 17, No. 31, 2011, pp. 8663-8670. <http://dx.doi.org/10.1002/chem.201003531>
 - [14] A. Dong, R. Tang and W. E. Buhro, "Solution-Based Growth and Structural Characterization of Homo- and Heterobranched Semiconductor Nanowires," *Journal of the American Chemical Society*, Vol. 129, No. 40, 2007, pp. 12254-12262. <http://dx.doi.org/10.1021/ja0737772>
 - [15] D. D. Fanfair and B. A. Korgel, "Twin-Related Branching of Solution-Grown ZnSe Nanowires," *Chemistry of Materials*, Vol. 19, No. 20, 2007, pp. 4943-4948. <http://dx.doi.org/10.1021/cm071440t>
 - [16] N. Petchsang, L. Shapoval, F. Vietmeyer, Y. Yu, J. H. Hodak, I.-M. Tang, T. H. Kosel and M. Kuno, "Low Temperature Solution-Phase Growth of ZnSe and ZnSe/CdSe Core/Shell Nanowires," *Nanoscale*, Vol. 3, No. 8, 2011, pp. 3145-3151. <http://dx.doi.org/10.1039/c1nr10176e>
 - [17] L. Zhang and H. Yang, "The Ag⁺ Induced Solution-Liquid-Solid Growth, Photoluminescence and Photocatalytic Activity of Twinned ZnSe Nanowires," *Applied Physics A: Materials Science & Processing*, Vol. 98, No. 4, 2010, pp. 801-810. <http://dx.doi.org/10.1007/s00339-009-5524-4>
 - [18] J. Wang, C. Yang, Z. Huang, M. G. Humphrey, D. Jia, T. You, K. Chen, Q. Yang and C. Zhang, "Seed-Catalyzed Heteroepitaxial Growth and Nonlinear Optical Properties of Zinc Selenide Nanowires," *Journal of Materials Chemistry*, Vol. 22, No. 19, 2012, pp. 10009-10014. <http://dx.doi.org/10.1039/c2jm00091a>
 - [19] J. Wang, K. Chen, M. Gong, B. Xu and Q. Yang, "Solution-Solid-Solid Mechanism: Superionic Conductors Catalyze Nanowire Growth," *Nano Letters*, Vol. 13, No. 9, 2013, pp. 3996-4000. <http://dx.doi.org/10.1021/nl400637w>
 - [20] Y. Cai, T. L. Wong, S. K. Chan, I. K. Sou, D. S. Su and N. Wang, "Growth Behaviors of Ultrathin ZnSe Nanowires by Au-Catalyzed Molecular-Beam Epitaxy," *Applied Physics Letters*, Vol. 93, No. 23, 2008, Article ID: 233107. <http://dx.doi.org/10.1063/1.3037024>
 - [21] Q. Li, X. G. Gong, C. R. Wang, J. Wang, K. Ip and S. K. Hark, "Size-Dependent Periodically Twinned ZnSe Nanowires," *Advanced Materials*, Vol. 16, No. 16, 2004, pp. 1436-1440. <http://dx.doi.org/10.1002/adma.200306648>
 - [22] A. Sahu, L. Qi, M. S. Kang, D. Deng and D. J. Norris, "Facile Synthesis of Silver Chalcogenide (Ag₂E; E = Se, S, Te) Semiconductor Nanocrystals," *Journal of the American Chemical Society*, Vol. 133, No. 17, 2011, pp. 6509-6512. <http://dx.doi.org/10.1021/ja200012e>
 - [23] R. de Ridder and S. Amelinck, "An Electron Microscopic Study of the Polymorphic Transformation in Ag₂Se (I)," *Physica Status Solidi A-Applications and Materials Science*, Vol. 18, No. 1, 1973, pp. 99-107. <http://dx.doi.org/10.1002/pssa.2210180106>
 - [24] Y. Saito, M. Sato and M. Shiojiri, "Orientation in Ag₂Se Polymorphic Films Produced by the Reaction of Silver Films with Selenium," *Thin Solid Films*, Vol. 79, No. 3, 1981, pp. 257-266. [http://dx.doi.org/10.1016/0040-6090\(81\)90314-X](http://dx.doi.org/10.1016/0040-6090(81)90314-X)
 - [25] S. T. Connor, C.-M. Hsu, B. D. Weil, S. Aloni and Y. Cui, "Phase Transformation of Biphasic Cu₂S-CuInS₂ to Monophasic CuInS₂ Nanorods," *Journal of the American Chemical Society*, Vol. 131, No. 13, 2009, pp. 4962-4966. <http://dx.doi.org/10.1021/ja809901u>
 - [26] C. Xiao, J. Xu, K. Li, J. Feng, J. Yang and Y. Xie, "Superionic Phase Transition in Silver Chalcogenide Nanocrystals Realizing Optimized Thermoelectric Performance," *Journal of the American Chemical Society*, Vol. 134, No. 9, 2012, pp. 4287-4293. <http://dx.doi.org/10.1021/ja2104476>

- [27] O. Tadanaga, Y. Koide, K. Hashimoto, T. Oku, N. Terauchi, Y. Tomomura, A. Suzuki and M. Murakami, "Dependence of Electrical Properties on Work Functions of Metals Contacting to p-Type ZnSe," *Japanese Journal of Applied Physics*, Vol. 35, No. 3, 1996, pp. 1657-1663. <http://dx.doi.org/10.1143/JJAP.35.1657>
- [28] C. Wang, S. Peng, R. Chan and S. Sun, "Synthesis of AuAg Alloy Nanoparticles from Core/Shell-Structured Ag/Au," *Small*, Vol. 5, No. 5, 2009, pp. 567-570. <http://dx.doi.org/10.1002/sml.200801169>
- [29] X. T. Zhang, K. M. Ip, Q. Li and S. K. Hark, "Photoluminescence of Ag-Doped ZnSe Nanowires Synthesized by Metalorganic Chemical Vapor Deposition," *Applied Physics Letters*, Vol. 86, No. 20, 2005, Article ID: 203114. <http://dx.doi.org/10.1063/1.1931828>
- [30] P. O. Holtz, B. Monemar and H. J. Loykowski, "Optical Properties of Ag-Related Centers in Bulk ZnSe," *Physical Review B*, Vol. 32, No. 2, 1985, pp. 986-996. <http://dx.doi.org/10.1103/PhysRevB.32.986>

Supplement

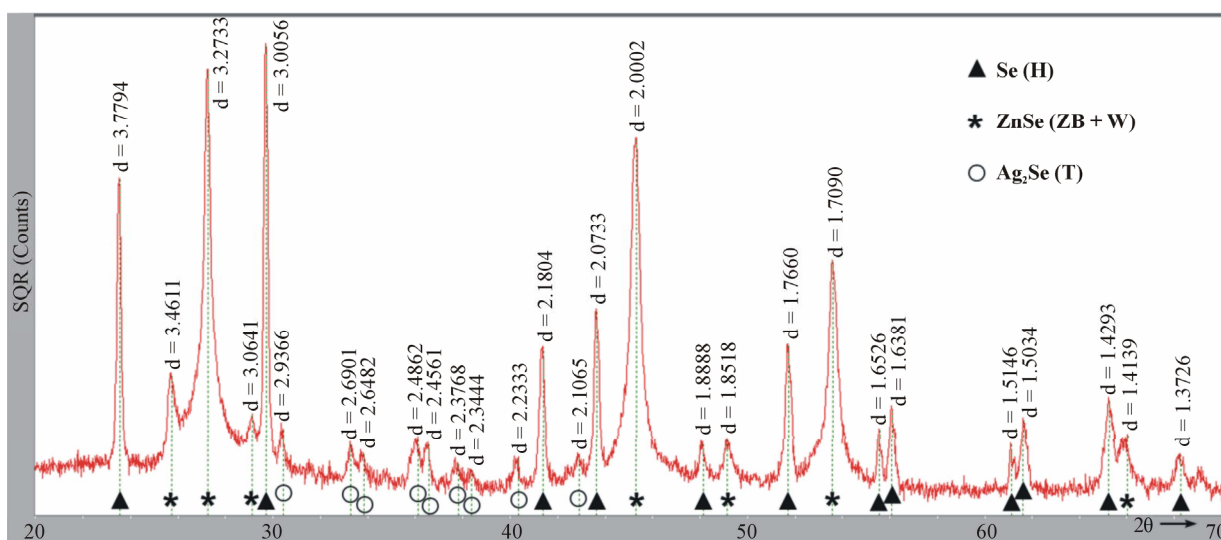


Figure S1. XRD pattern of ZnSe nanowires prepared from 5% Ag/Zn molar ratio at 200°C for 1 h. The peaks in the pattern match well with diffractions from Se (Hexagonal, JCPDS# 86-2246), ZnSe (ZB + W, JCPDS# 88-2345, 89-2940), and Ag₂Se (Tetragonal).

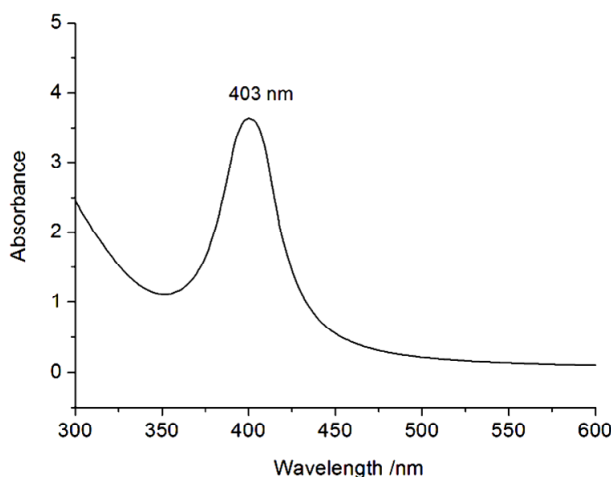


Figure S2. UV-Vis absorption spectrum of Ag nanoparticles reduced by oleylamine in the mixture reaction solution of oleic acid (5 mL) and oleylamine (1 mL) at 180°C for 20 min. The absorption peak loaded at 403 nm is due to the surface plasmon resonance (SPR) of Ag.