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**Document Version:** 

Accepted author manuscript (peer-reviewed)

Citation for published version: Rothman, A, Forsht, T, Danieli, Y, Popovitz-Biro, R, Rechav, K, Houben, L & Joselevich, E 2018, 'Guided Growth of Horizontal ZnS Nanowires on Flat and Faceted Sapphire Surfaces', Journal of Physical Chemistry C, vol. 122, no. 23, pp. 12413-12420. https://doi.org/10.1021/acs.jpcc.8b04063

Total number of authors:

**Digital Object Identifier (DOI):** 10.1021/acs.jpcc.8b04063

Published In: Journal of Physical Chemistry C

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# Guided Growth of Horizontal ZnS Nanowires on Flat and Faceted Sapphire Surfaces

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#### Abstract

The surface-guided growth of horizontal nanowires (NWs) allows assembly and alignment of the NWs on the substrate during the synthesis, thus eliminating the need for additional processes after growth. One of the major advantages of guided growth over post-growth assembly is the control on the NWs direction, crystallographic orientation and position. In this study, we use the guided growth approach to synthesize high-quality, single-crystal, aligned horizontal ZnS NWs on flat and faceted sapphire surfaces, and show how the crystal planes of the different substrates affects the crystal structure and orientation of the NWs. We also show initial results of the effect of Cu doping on their photoluminescence. Such high-quality aligned ZnS NWs can potentially be assembled as key components in phosphorescent displays and markers due to their unique optical properties. The ZnS NWs have either wurtzite or zinc-blende structure depending on the substrate orientations and contain intrinsic point defects such as sulfur vacancies, which are common in this material. The crystallographic orientations are consistent with those of guided NWs from other semiconductor materials, demonstrating the generality of the guided growth phenomenon. The successfully grown ZnS NWs and the Cu doping are the first step toward fabrication of optoelectronic devices based on ZnS nanostructures.

### Introduction

Semiconductor nanowires (NWs) are important building blocks for future nanotechnology<sup>1</sup>. Owning to their controlled size and properties, NWs are especially promising for potential applications in nanoelectronics<sup>2-3</sup>, photonics<sup>4-5</sup> and sensing devices<sup>6-7</sup>. Growing NWs requires addition of material during the growth process along only one direction. One of the most common methods to synthesize NWs is the vaporliquid-solid (VLS) method, which was first described in 1964 by Wagner and Ellis<sup>8</sup>. The VLS growth mechanism is based on the directional growth of the semiconductor material from a metallic nanoparticle acting as a catalyst. The grown NWs can be formed either vertically, horizontally or tilted relative to the substrate, and can grow in oriented arrays or randomly. One of the major challenges of NWs is their integration into practical devices. Several techniques offered large-scale aligning and assembling of NWs on the substrate, such as assembly with liquid flows<sup>9</sup>, electric fields<sup>10</sup>, mechanical shearing<sup>11</sup> and Langmuir-Blodgett compression<sup>12</sup>. Yet, these post-growth routes can be problematic because the alignment of the NWs is subject to thermal and dynamic fluctuations, and the brittle NWs are usually damaged and contaminated during the process.

A different approach for integrating the NWs is based on their horizontally guided growth directed by the substrate<sup>13</sup>, as previously shown also for carbon nanotubes<sup>14-18</sup>. Various semiconducting materials such as GaN<sup>13, 19-21</sup>, ZnO<sup>22-24</sup>, ZnSe<sup>25-26</sup>, ZnTe<sup>27</sup>, CdSe<sup>28</sup>, CdS<sup>29-30</sup> and CsPbBr<sub>3</sub><sup>31</sup> were grown into aligned NW arrays, guided by epitaxial and graphoepitaxial relationships with the substrate. The epitaxial growth is usually driven by

the minimization of the mismatch between the NW and the substrate, which controls the growth along specific lattice directions and crystallographic orientation (Figure. 1a-d), while the graphoepitaxial growth is driven by maximization of the interface area between the NW and substrate and the NWs are directed and grow along the faceted surface of the substrate, such as nanosteps or nanogrooves (Figure. 1e-f). The guided NWs growth enabled fabrication of aligned arrays of high-performance electronic and optoelectronic devices, including transistors<sup>27</sup>, logic circuits<sup>23</sup>, photodetectors<sup>28</sup> and photovoltaic cells<sup>26</sup>.

ZnS is an important II-VI semiconductor with direct wide-bandgap and two stable polymorphs: zinc-blende (ZB) with a bandgap of 3.72 eV and wurtzite (WZ) with 3.77  $eV^{32-33}$ . ZnS has been extensively studied due to its unique optical properties and is used in photonic applications such as cathode ray tubes (CRT)<sup>34</sup>, displays<sup>35-36</sup> and sensors<sup>37</sup>. Longlasting phosphorescence can be also achieved by doping the ZnS with metallic ions such as Cu, Mn, and Eu<sup>38-40</sup> which create additional radiative transitions. For example, the green luminescence due to Cu doping is due to a transition from the conduction band of ZnS to the  $t_2$  level of excited Cu<sup>+2</sup> ( $d^9$ ) in the ZnS band gap <sup>41</sup>. The ZnS properties can be tuned through control of its crystal structure, dopants, size and morphology. Specific interest was given to ZnS nanostructures. ZnS quantum dots show different and enhanced optical properties compared to the bulk ZnS<sup>42-43</sup> and one-dimensional (1D) nanostructures such as nanowires<sup>44-46</sup>, nanobelts<sup>47-48</sup>, nanoribbons<sup>49</sup> and nanotubes<sup>50</sup> of ZnS showed tunable optoelectronic properties. Various approaches for the growth of ZnS nanostructures were studied, including solution synthesis<sup>51</sup>, laser-ablation catalytic growth<sup>52</sup> and chemical vapor deposition (CVD)<sup>38-39</sup>. Recent studies demonstrated the growth on ZnS NWs on silicon<sup>38</sup>, <sup>53-55</sup>, sapphire<sup>56</sup>, and zinc foils<sup>57</sup>, focusing on their crystal structure and optical properties, but so far only vertical NWs were observed, and not their horizontally guided growth has not been reported. Since it is not obvious that every material should grow as horizontally guided NWs, it is important to demonstrate that ZnS can also do it. Expanding the generality of the guided growth phenomenon to different materials is important for the understanding of the phenomenon. Moreover, every material has different epitaxial relationships with different substrates, leading to NWs with often unexpected crystal structures and crystallographic orientations for each specific plane of a single-crystal substrate. A survey of these epitaxial and graphoepitaxial relations and crystallographic data for guided NWs of a specific composition on different surfaces of a substrate is important for their subsequent integration into devices <sup>23, 25, 27-30</sup>, and more complex structures such as core-shell guided NWs<sup>26</sup>.

Herein we report for the first time the surface-guided growth of horizontal singlecrystal ZnS NWs. The NWs were grown epitaxially and graphoepitaxlly on various sapphire substrates, including C (0001) ,R ( $1\overline{1}02$ ) and annealed M ( $1\overline{1}00$ ), where they display different crystal phases and crystallographic orientations In addition, Cu-doped ZnS powder was used to grow Cu-doped ZnS guided NWs. The latter results could be used to design other nanostructures (e.g. core-shell heterostrucures, doped NWs, etc.) , a basis for devices (e.g. LEDs, transistors, photodetectors, photovoltaic cells, etc.) and for further applications as phosphorescent displays and markers.



**Figure 1:** Guided VLS growth of horizontal ZnS NWs. Schematic illustration of guided NWs on (a) C-plane sapphire, (c) R-plane sapphire and (e) annealed M-plane sapphire. SEM images of ZnS NWs: epitaxial growth on (b) C-plane sapphire and (d) R-plane sapphire and graphoepitaxial growth on (f) annealed M-plane sapphire. The blue indices and vectors describe the sapphire crystallographic directions.

#### **Materials and Methods**

#### Nanowires synthesis

The NWs were synthesized on sapphire wafers (Roditi International, Inc.) with three different orientations (C-, R- and M- planes). The M-plane wafer was annealed before the synthesis at 1600°C in air for 10 hours using high-temperature tube furnace. The NWs were grown from dispersed gold nanoparticle solution and gold catalyst pattern in order to achieve long arrays. The patterning was done by a conventional photolithography process (MA/BA6 Karl-Suss mask aligner) with negative photoresist (NR-9 1000PY) and suitable masks. A gold (Holland Moran, 99.999%) thin film of 5Å thickness was deposited using electron-beam physical vapor deposition system (Telemark), followed by lift-off in acetone. Prior to the synthesis, the substrates were heated to 550°C for 7 min.

The ZnS NWs were synthesized in a three-zone tube furnace (Lindberg Blue M, Thermo Scientific). The ZnS source was ZnS powder (Sigma Aldrich, 99.99%). The tube was purged with N<sub>2</sub> (Gordon Gas, 99.999%) and H<sub>2</sub> (Parker Dominic Hunter H<sub>2</sub> generator, 99.99995%) 490:12 sccm mixture and 400 mbar and the sapphire substrates were placed downstream on a quartz slide. The temperature of the ZnS source powder was held at 960 °C and the sapphire substrates were held at 780 °C. The typical growth time was 15-20 minutes.

Cu-doped ZnS powder was used for synthesizing Cu-doped ZnS guided NWs with the same procedure as for undoped ZnS NWs. The Cu-doped ZnS powder was prepared from 0.1 gr of CuCl<sub>2</sub>·H<sub>2</sub>O powder (BDH Laboratory Reagents, 98%) was heated to 70° C for 10 minutes and later was mixed with 0.5 gr of ZnS powder (Sigma Aldrich, 99.99%). The mixture was cooled down to room temperature prior to the NWs synthesis.

#### Structural characterization

The morphology of the ZnS NWs was studied using Scanning Electron Microscope (SEM, Zeiss Supra 55VP FEG LEO). In order to study the crystallographic structures and orientations, focused-ion-beam (FIB, FEI Helios 600 dual beam microscope) was used to cut thin lamellae across the NWs. The NWs cross-sections were examined by high-resolution transmission electron microscope (HRTEM, FEI Tecnai F30). The HRTEM images were analyzed using Fast Fourier transform (FFT) from selected areas across the NWs and the substrate. Chemical analysis was performed by Scanning Transmission Electron Microscope – Electron Energy Loss Spectroscopy (STEM-EELS, FEI Tecnai F30) equipped with a Gatan imaging filter).

#### **Optical characterization**

Photoluminescence (PL) measurements were conducted using a micro-Raman/micro-PL system (Horiba LabRAM HR Evolution). A 325 nm He–Cd laser was focused on the NWs through a 40x objective lens.

#### **Results and Discussion**

The study of undoped ZnS guided NWs was carried out on three different sapphire surfaces: the flat planes C (0001) and R ( $1\overline{1}02$ ) to demonstrate the epitaxially guided growth and the faceted plane M ( $1\overline{1}00$ ) to demonstrate the graphoepitaxial guided growth. On all the planes, the NWs are guided and well aligned having a nearly squared crosssection with rounded corners (Figure 2b, 2e, 2h and 2j). The NWs have a gold droplet at their ends, as can be seen in Figure 2g, which a strong indication of VLS tip-growth mechanism. The NWs have a typical thickness of 10-60 nm with a length of 2-50 µm. The crystallographic orientation and the growth direction of the grown NWs varied with the orientations of the sapphire substrates, as summarized in Table 1 and detailed in the next paragraphs. All the cross-section TEM images of the examined NWs are presented in the Supporting Information (Figure S1-S3).

Guided growth of ZnS NWs on flat sapphire surfaces. On C (0001) sapphire, the guided ZnS NWs grow along six isoperiodic M  $\langle 10\bar{1}0 \rangle$  directions of the sapphire, as can be seen in Figure 1b, which are defined by the three-fold symmetry of the C plane, as previously was shown for ZnSe<sup>25</sup>, ZnTe<sup>27</sup>, CdSe<sup>28</sup> and CdS<sup>29</sup> guided NWs. The ZnS NWs have WZ crystal structure with growth axis direction along the [ $\bar{1}100$ ] direction and a transversal plane of ( $\bar{1}\bar{1}20$ ) which are the same for the sapphire ( $11\bar{2}0$ ) (Figure 2c). In this case the mismatch, which is defined as the ratio between the lattice constants of the NW and the substrate, is dominant, and determines the crystallographic orientation of the NWs as was shown before for most other guided semiconductor NWs on sapphire reported so far <sup>13, 19-20, 22, 25-29, 58</sup>, except CsPbBr<sub>3</sub><sup>31</sup>. This mismatch induces strain that is relieved by misfit dislocations. The transversal mismatch, which is the ratio between the sapphire and ZnS NW lattice constant difference and the sapphire lattice constant in the direction transversal to the NW long axis, was calculated to be 0.51%, which is also compatible with the observation of misfit dislocations.



**Figure 2**: Guided growth of horizontal ZnS NWs on various sapphire planes. The first row (a, b and c) represents the epitaxial growth on C-plane. The second row (d, e, and f) represents the epitaxial growth on R-plane and the third row (g, h, i, j and k) represents the graphoepitaxial growth on annealed M-plane. SEM

images are on (a), (e) and (g). Cross-sectional HRTEM images are on (b), (e) (h) and (j). Magnification of the NW-surface is on (c), (f) (i) and (k). For each substrate orientation the blue indices, vectors and bars describe the Sapphire crystallographic orientations whereas the yellow ones describe the ZnS crystallographic orientations. The insets are the FFT images of the NW.

The growth of ZnS NWs on R (1102) sapphire is along 4 different directions  $\pm [20\overline{2}\overline{1}]$ and  $\pm [02\overline{2}1]$  of the sapphire substrate, separated by 94° and 86° angles, as can be seen in Figure 1d. Similar to the NWs that grow on the C-plane, these NWs also have WZ structure, but with growth axis along the polar [0001] crystallographic orientation. The observed growth directions on the sapphire substrate are similar to those that were demonstrated for ZnSe<sup>25</sup> and CdSe<sup>28</sup> guided NWs but different from those that were found on GaN<sup>13</sup> and ZnO<sup>22</sup> guided NWs. For ZnTe<sup>27</sup> NWs no guidance was observed on R-plane Sapphire at all. This comparison indicates that the guided growth phenomenon is not only substratedependent but may be affected by the grown material itself and its relation to the substrate. In general, each combination of NW material and substrate has been found to prefer to grow along a specific lattice direction of the substrate, the NWs having one or a few specific crystallographic orientation <sup>13</sup>. The epitaxial relationship between the NW material and the substrate is not sufficient to determine the preferred growth direction. For instance, ZnO NWs on M-plane sapphire can grow in two perpendicular directions of the substrate with respectively perpendicular crystallographic orientations both keeping the same epitaxial relationship, depending on the NW diameter <sup>22</sup>. This thickness dependence has been attributed to the minimum thickness for misfit dislocations, which are an efficient mechanism of strain relaxation. The surface energy of the NW facets may also play a role in determining the preferred direction and crystallographic orientation of guided NWs. These different orientations have been studied in detail by means of second-harmonic generation polarimetry <sup>24</sup>. In the case of guided ZnS NWs on R-plane sapphire, the transversal mismatch was calculated to be 2.62%, which is also compatible with the observation of misfit dislocations.

Guided growth of ZnS NWs on faceted sapphire surfaces. Flat M ( $1\overline{1}00$ ) sapphire is a thermodynamically unstable plane with relatively high surface energy<sup>59</sup>. Upon thermal treatment at elevated temperature (1400–1600 °C), the M-plane surface undergoes restructuration and present the more thermodynamically stable S-plane ( $10\overline{1}1$ ) and Rplane  $(1\overline{1}02)$  in periodically faceted V-shaped nanogrooves (Figure 2h, 2i, 2j and 2k). The guided ZnS NWs grow along these nanogrooves in the two directions  $\pm [\overline{1}\overline{1}20]$  of the sapphire (Figure 1f). The ZnS NWs in this case have either WZ or ZB crystal structure with growth axis direction along the  $[11\overline{2}0]$  and [110] directions, respectively, as was previously observed<sup>26</sup>. This may be attributed to the need of the NWs to adapt simultaneously to two different planes and their respective energetic constrains. Unlike the growth of the NWs on the flat surfaces, here the growth is guided by the graphoepitaxial effect and dominates over the epitaxial effect, as observed for other materials<sup>13, 22, 25-28</sup>. No intermixing of crystal polytypes was observed within the same ZnS NWs. The crystallographic structure of the examined NWs was retrieved by analyzing the FFT images of the HRTEM images, and the analysis of all the NWs showed clear correlation to the theoretical diffraction pattern pointing on single crystal with one type of structure.

**Table** 1: Crystallographic orientation and growth direction of guided ZnS NWs grown on different sapphire
 planes. For the epitaxial growth the calculated lattices mismatch is added.

Substrate Orientation	# of growth directions	# of NWs	Crystal phase	Horizontal ZnS  sapphire	Transversal ZnS  sapphire	Axial direction ZnS  sapphire	Transversal Mismatch (%)
C-plane (0001)	6	5	WZ	(0001)   (0001)	(1120)   (1120)	[ <b>1100</b> ]  [1100]	0.51
$\begin{array}{c} \text{R-plane} \\ (1\overline{1}02) \end{array}$	4	4	WZ	(1210)   (1102)	(1010)   (1104)	[ <b>0001</b> ]  [202 <u>7</u> ]	2.62
Annealed M-plane	2	4	WZ			[ <b>11</b> 20]   [1120]	
		4	ZB			[ <b>110</b> ]   [11 <b>2</b> 0]	

**Compositional Analysis of Guided ZnS NWs.** Elemental composition and mapping of the ZnS NWs were conducted using Electron Energy Loss Spectroscopy (EELS) and Energy-Filtered Transmission Electron Microscopy (EFTEM) and were carried out on cross-section samples of NWs grown on annealed M-plane sapphire. Quantitative analysis based on the EELS spectra (Figure S4, Supporting Information) revealed a 1.00: 0.88 atomic ratio of Zn and S, respectively. Elemental mapping for Zn, S, and O by EFTEM (Figure 3) revealed sharp ZnS-sapphire interfaces without observable interdiffusion, and homogeneous NW with uniform distributions of the Zn and S. It should also be noted that a small amount of O was detected as a thin layer around the NW itself (Figure 3 O map). However, the EELS quantitative analysis from the NW itself showed less than 5 at. % of Oxygen.



**Figure 3**: EFTEM elemental map analysis of a guided ZnS NW on annealed M-plane sapphire. The zero loss image, Zinc (blue), Sulfur (yellow) and Oxygen (red) maps are presented.

**Optical characterization of guided ZnS NWs.** Room-temperature PL spectra were obtained under excitation at 325 nm using a He-Cd laser. Typical PL spectra of a single ZnS NW on C-plane and annealed M-plane substrates and of the sapphire are presented in Figure 4. The analysis of the ZnS spectrum can be divided into two main regions of interest: the 325-350 nm region and the 400-600 nm region. The main peak in the first region for the NW grown on the C-plane was fitted to a Lorentzian with maximum of 336 nm (3.69 eV), for the NW grown on the annealed M-plane it was 349 nm (3.55 eV). This difference can be qualitatively attributed to the result that on C-plane sapphire the ZnS

NWs have a WZ structure (bulk band gap 3.77 eV<sup>32</sup>) whereas on M-plane they can have WZ or ZB structures (bulk ZB band gap  $3.72 \text{ eV}^{33}$ ), because these peaks represent the near band-emission (NBE) of the NWs. Quantitatively, the NBE maxima on each plane are redshifted compared to the band gap of bulk WZ and ZB ZnS by 0.08 eV and 0.17 eV, respectively. These slight shifts may be attributed to compressive strain induced in the NWs. Red shift as a result of quantum confinement effect is not expected due to the small Bohr radius of the exciton for ZnS of 2.5 nm<sup>60</sup>, which is significantly smaller than the diameter of the NWs. Six very sharp peaks appear on the envelope of the main NBE peak for both spectra at 328, 332, 336, 340, 344 and 348 nm. These peaks are identified as the first, second, third, fourth, fifth and sixth orders of the Raman longitudinal optical phonons (LO) modes, respectively, as was observed previously for  $ZnS^{61}$ . The appearance of the LO mode Raman peaks was reported to have the highest intensities in ZnS WZ structure<sup>62</sup> and it correlates with the concentration of defects in the NW. Moreover, the red shift of the LO Raman peaks in this nanostructure system can also be attributed to tensile stress due to the presence of these defects<sup>63-64</sup>.

The broad peak in the second region for the NW grown on the C-plane was fitted to three Lorentzians, yielding maxima at 463, 497 and 533 nm, while for the NW grown on the annealed M-plane the broad peak fit to maxima at 441, 505 and 589 nm. The luminescence in the blue emission region (463- 505 nm) is associated with trapped luminescence arising from S vacancies or O impurities<sup>65</sup> that diffused from the thin oxide layer observed around the NW (Figure 3 oxygen map). This result correlates with the chemical analysis measurement discussed above, that the NWs contains less Sulfur than Zinc. The emission within the green region is attributed to dopant or impurity atoms. Wang et al.<sup>66</sup> suggested that the emission at 520-540 nm is attributed to Au<sup>+</sup> ions substituting the

 $Zn^{2+}$  ions formed as a result of Au diffusion from the Au catalyst droplet into the NW. Our EELS spectra do not indicate presence of Au within sensitivity range (Au concentration < 0.01 at. %). Other than this broad PL peak at 463-505 nm, which could also be attributed to S vacancies or O impurities, as mentioned above, we currently have no evidence of Au presence in the ZnS NWs. The peaks in the 657-680 nm in both spectra are attributed to ZnS Raman peaks. The sharp peaks in 325 and 650 nm appeared in the NW and sapphire spectra and are the first and second harmonic of the exciting laser.



**Figure 4:** Typical room-temperature photoluminescence spectrum of a single ZnS NW on C-plane (red line) , annealed M-plane (blue line) and of bare sapphire substrate (black line), excited by 325 nm laser.

**Guided growth of Cu-doped ZnS NWs.** In order to examine the possibility of utilizing the unique phosphorescent property of ZnS, doping the guided ZnS NWs was conducted. Metal doping can be achieved by several techniques <sup>60, 67-68</sup> We chose to do it by mixing Cu salts in the ZnS powder source during the synthesis. The guided Cu-doped ZnS NWs grow graphoepitaxialy along the nanogrooves on the annealed M-plane surface

in the  $\pm [\overline{1}\overline{1}20]$  directions of the sapphire similar to the undoped guided ZnS NWs, as can be seen in the UV-light optical image in Figure 5b. Room-temperature PL spectra were obtained under excitation by a 325 nm He-Cd laser, same as for undoped ZnS NWs. Typical PL spectra of a Cu- doped single ZnS NW compared to an undoped ZnS NW on annealed M-plane are presented in Figure 5a. The main difference is the appearance of the blue peak at 441 nm in the Cu-doped NW. This peak is not the expected main green peak for Cu doping but is attributed to an emission center formed by the spatial association of a substitutional Cu atoms<sup>53</sup> which is characteristic of Cu-doped ZnS. This peak is also close to the defect-related emissions in the ZnS NW, as was discussed previously. The additional emission in the 672 nm may be assigned to the split transition between the deep localized donor levels to t levels of the Cu dopant  $^{41}$ . Time-resolved measurements of low-intensity emission, which are not available at present in our lab, would be needed to determine if the additional emission peaks in the Cu-doped ZnS NWs are related to a slow phosphorescence or fast photoluminescence. In addition, doping by Cu and other metals could be performed by using the desired metal as a catalyst instead of Au.





**Figure 5:** (a) Room-temperature photoluminescence spectrum of a single Cu-doped ZnS (black line) and undoped ZnS (dashed line) NWs grown on annealed M-plane sapphire. (b) Optical image of the Cu-doped ZnS under UV laser illumination.

### Conclusions

In this paper, we demonstrated the guided growth of aligned VLS ZnS NWs on flat and faceted sapphire substrates by epitaxy and graphoepitaxy, respectively. The guided NWs are all single-crystal with a nearly squared cross-section. Depending on the substrate orientation, the NWs show polar or non-polar crystallographic orientations, and exhibited WZ structure when grown epitaxially on C- and R-plane sapphire, and either WZ or ZB structure when grown graphoepitaxially on annealed M-plane sapphire. Chemical analysis revealed high purity ZnS NW with slightly less sulfur than zinc. The optical characterization confirmed the WZ structure and correlated to the chemical analysis results of sulfur vacancies and a thin oxide layer of the NW facets that are exposed to ambient air after growth. Preliminary doping of the ZnS NWs was conducted using Cu, presenting additional emissions peaks. The guided growth of Cu-doped ZnS NWs with additional optical transitions is promising toward potential applications of phosphorescent NW arrays. The overall results, combined with similar ones for other materials, demonstrate the generality of the guided growth approach for the large-scale integration of NWs into devices.

## **Supporting Information**

Cross-section TEM images and crystallographic orientation of the examined NWs, EELS compositional analysis of the guided ZnS NWs.

# Acknowledgements

This research was supported by the European Research Council (ERC) Advanced Grant

(No. 338849). E.J. holds the Drake Family Professorial Chair of Nanotechnology.

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# **TOC Graphic**

